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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE PATENTS

Applicant(s): Donald R. Huffman et al. Examiner: P. DiMauro

Serial No.: 08/236,933

Art Unit: 1103

Filed: May 2, 1994

Docket: 7913zazy

For: NEW FORM OF CARBON

Assistant Commissioner for Patents  
Washington, DC 20231SUPPLEMENTAL DECLARATION OF HAROLD W. KROTO UNDER  
37 C.F.R. §1.132

I, HAROLD W. KROTO, PH.D., declare and say as follows:

1. I am the Royal Society Research Professor in the School of Chemistry and Molecular Sciences at the University of Sussex, Brighton, United Kingdom (one of only twenty such appointments in the United Kingdom). In addition, I have been awarded over one dozen honorary degrees from various universities. In 1996, I, along with Robert Curl and Richard Smalley, received the Nobel Prize in Chemistry for our discovery of fullerenes. Earlier that year, I was also awarded Knighthood for my contributions to chemistry. For the convenience of the United States Patent and Trademark Office, I have attached hereto as Exhibit 1 my curriculum vitae, which describes my credentials and demonstrates my expertise in the area of fullerenes.

2. I am intimately familiar with the literature concerning and was personally involved in the search for  $C_{60}$  and other fullerenes. I have written several articles on the

subject, as evidenced by the publications listed in Exhibit 1, including the first definitive and only complete review on the subject in Kroto, et al., in Chemical Review 1991, 91, 1213 - 1235. I therefore believe that it is fair to say that I am among the recognized experts on the subject of fullerenes.

3. This Declaration supplements and is not intended to replace the previous Declarations which were executed on July 27, 1995 and June 9, 1995, the contents of which are incorporated herein by reference.

4. I have been requested by applicants' attorney to read and review the above-identified application, i.e., USSN 08/236,933 and the pending claims therein. In addition, I have been requested by applicants' attorney to comment on my understanding of the terms "macroscopic amounts" as applied to fullerenes, including  $C_{60}$ , in the claims and to comment on whether, in my opinion, the underlying specification clearly describes a process for making fullerenes, including  $C_{60}$ , in macroscopic amounts without an undue amount of experimentation.

5. As requested, I have read and reviewed the above-identified application, including the pending claims in the above-identified application. It is my understanding that the claims in the above identified application are directed, among other things, to a process of producing  $C_{60}$  in macroscopic amounts.

6. I have been advised that there is a companion application, USSN 486,669, on file in the United States Patent

and Trademark Office. I have been advised that, except for the claims, the disclosure in the '669 application is identical to that of the above-identified application. I have also reviewed the pending claims related thereto. It is my understanding that these claims are directed, among other things, to a process for making fullerenes in macroscopic amounts.

7. I have also been advised of the existence of two more applications, namely USSN 580,246 and USSN 471,890. It is my understanding that the former application is directed to, among other things,  $C_{60}$  in macroscopic amounts, while the latter is directed to, among other things, fullerenes in macroscopic amounts. It is also my understanding that, except for the claims, the respective specifications are not only identical, but also are identical to the specification of the above-identified application.

8. It is my opinion that the above-identified specification describes the preparation of fullerenes, including, for example,  $C_{60}$ , in macroscopic amounts. This is based upon my understanding of the application and my repetition of the procedure described in the underlying application for producing fullerenes, including  $C_{60}$ , and isolation thereof in macroscopic amounts.

9. It is my opinion that the term "macroscopic amounts" as used in the claims is clearly understood by the ordinary skilled artisan. It is my understanding that the term is being used in its plain and ordinary meaning to connote that

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a process for making fullerenes, including  $C_{60}$ , by (1) vaporizing graphite rods in a conventional bell jar evaporator in the presence of an inert quenching gas, e.g., helium or argon, to produce carbon smoke; (2) collecting the smoke formed; (3) then extracting the fullerenes, including  $C_{60}$ , using benzene, or other inert solvent; (4) then, after evaporating the solvent, subliming the impure product; and (5) then collecting the sublimed product.

12. The specification on Pages 3-8 describes a more general process for preparing fullerenes, including  $C_{60}$ , and describes other means for extracting fullerenes, including  $C_{60}$ , from the smoky carbon product, including sublimation and the use of other non-polar solvents to extract the fullerenes, including  $C_{60}$ , from the smoky carbon product.

13. It is my opinion that a person of ordinary skill in the art in 1990 reading the specification would understand the specification to be directed to the class of carbon structures that have come to be commonly referred to as fullerenes. There is no question that the specification describes, among other things,  $C_{60}$  and  $C_{70}$ , which are designated as fullerene-60 and fullerene-70, respectively. These are species of fullerenes, and the skilled artisan would comprehend that the specification is directed to fullerenes. Moreover, spectral data, especially mass spectra data of the smoky carbon product produced from the vaporization of the elemental carbon in the inert quenching gas, in accordance with the procedure

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described in the above-identified application, reveals that the smoky carbon product contains other species of fullerenes; although not in the abundance of fullerene-60 or fullerene-70 nevertheless, collectively in macroscopic amounts in the soot. Moreover, at the time of September 1990, various other hollow caged species containing solely carbon atoms, now known as fullerenes, had been postulated. So even if not specifically mentioned in the application, these other species of fullerenes were inherently present in the carbon soot produced by the process described in the underlying application -- a fact verified by experimentation. Consequently, it is my opinion that the ordinary skilled artisan in 1990 would understand that the above-identified specification is directed to, among other things, a process for making fullerenes, including  $C_{60}$ .

14. Moreover, it is my opinion that the ordinary skilled artisan in September 1990 reading the specification would understand that the teachings therein were applicable for preparing and isolating not only  $C_{60}$  and  $C_{70}$ , but also other fullerenes without an undue amount of experimentation. Thus, the above-identified application paves the road for preparing and isolating other fullerenes species without an undue amount of experimentation.

15. Moreover, the specification provides evidence in several instances that the inventors had produced the fullerene products, including  $C_{60}$ , in macroscopic amounts. For example, attention is directed to Example 1 which describes the product

18. Moreover, by following the procedure described in the above-identified application, and in accordance with the procedure outlined in Paragraph 17 herein, <sup>We</sup> have isolated fullerenes in macroscopic amounts, as defined herein. For

example, utilizing the procedure outlined in Paragraph 17, I have found that the smoky carbon product contains 5 to 10%  $C_{60}$  and 1%  $C_{70}$ . We routinely produce the soot in 1-5 gram quantities and routinely extract 100-500 milligram amounts batchwise. Thus, one kilogram of sooty carbon product produces, on average, 100g of  $C_{60}$ , 10g of  $C_{70}$  and 1 gram of other fullerenes, such as those indicated hereinabove. The various fullerenes formed can and are isolated in accordance with the isolation and purification procedures described in the above-identified application, without an undue amount of experimentation. Furthermore, the various fullerenes are isolated as solids, which are easily visible to the naked eye. For example, in a typical experiment conducted according to the procedure described in the above-identified application,  $C_{60}$  is formed in about 100 mg quantities  $C_{70}$  in about 10 mg quantities and the remainder in about 1 mg quantities.

19. Thus, by following the procedure described in the above-identified application, I have found that the process described therein inherently produces several species of fullerenes, including  $C_{60}$ , in macroscopic amounts. In fact, by following the procedure of Kratschmer and Huffman, outlined in the above identified application, crystalline material of fullerenes, including  $C_{60}$ , is produced which can be seen with the naked eye.

20. Moreover, there is additional evidence to support the statements made in Paragraph 19.



21. Attention is directed to an article by Kratschmer, et al. in Nature, 347, No. 6391, pp. 354-358 (1990), attached hereto as Exhibit 3. It was the first publication that describes the preparation and isolation of macroscopic amounts of a compound, e.g.,  $C_{50}$  and  $C_{70}$ , having the fullerene structure.

22. It is interesting to note there are over 3,390 publications referring to their Nature article. Only a handful of papers in some fifty years of science receive this number of citations. It is apparent that the Nature article has been cited an innumerable number of times because various scientists have followed the procedures described therein to successfully produce macroscopic quantities of fullerenes, including  $C_{60}$ . The fact that several thousand publications reference the Nature article for preparing fullerenes adds further support that the procedure described in the Nature article and thus the present specification provides sufficient information for the skilled artisan to generally make macroscopic amounts of fullerene, including  $C_{60}$ , without an undue amount of experimentation. Moreover, it is also attributable to the due recognition by the scientific community of Kratschmer's and Huffman's claim to have originated this method of production.

23. The realization by Huffman and Kratschmer of macroscopic quantities of fullerene and the isolation and characterization of  $C_{60}$  and  $C_{70}$  by the methods described in the above-identified application is recognized by the knowledgeable

scientific community as a long awaited and much needed breakthrough; it was surprising that relatively high yields of fullerene such as  $C_{60}$  could be achieved by these methods, as it was generally expected that infinitesimal amounts of fullerenes would exist in the soot product and that it would require very sophisticated equipment to isolate quantities of material required to establish and confirm the existence of the products. The difficulties that existed in the quest for  $C_{60}$  are well elaborated in the article entitled "Fullerenes" by Robert F. Curl and Richard E. Smalley, printed in Scientific American, Oct. 1991, pp. 54-62 attached hereto as Exhibit 4.

24. Although the discovery described in the Huffman and Kratschmer application may seem simplistic to the uninformed, especially in hindsight, their discovery was quite remarkable. The Kratschmer and Huffman method described in the above-identified application is all the more remarkable for the fact that so simple a procedure so readily produces large amounts of fullerenes. This is readily appreciated if one considers the historical perspective. Even since the detection of  $C_{60}$  by the collaborative efforts of the Smalley and Kroto groups in 1985, as described in the article in Nature, 1985, 318, 162-163, attached hereto as Exhibit 5, experts, such as Drs. Smalley and myself, both together and separately worked to prepare fullerenes on a larger scale. For five long years, many attempts were tried, but each was unsuccessful. Finally, to my expert knowledge, one group, Huffman and Kratschmer, was

the first to find and publish a methodology capable of producing and isolating fullerenes, such as  $C_{60}$ , in macroscopic amounts. This methodology is described in their application and satisfied a long felt need in this area.

25. Furthermore, one should not underestimate the significance of their discovery. For the first time, scientists were able to produce and work with samples of fullerenes. They were able to confirm the theoretical prediction about fullerenes and continue to explore new properties of same. Their discovery spawned enormous scientific interest, as evidenced by the 3390 citations to the Nature article in Exhibit 3 for making fullerenes. As a consequence, innumerable investigations and studies relating to fullerenes were conducted, generating several thousand publications on the subject. In short, I cannot emphasize enough that their discovery revolutionized the area of fullerenes by making it possible for experimental researchers worldwide to study their chemical and physical properties.

26. The scientific community has unanimously and unequivocally acknowledged and recognized that Kratschmer and Huffman have developed a process for preparing fullerenes, e.g.,  $C_{60}$ , in macroscopic amounts, and in consequence thereon has presented them with several awards. Even the press release by the Royal Swedish Academy of Sciences regarding the Nobel Prize in Chemistry in 1996, attached hereto as Exhibit 6, recognizes the contribution of Huffman and Kratschmer by

acknowledging that they for the first time produced "isolable quantities of  $C_{60}$ ". (See Page 2 of Exhibit 6). As stated in the press release:

[t]hey obtained a mixture of  $C_{60}$  and  $C_{70}$ , the structures of which could be determined...The way was thus open for studying the chemical properties of  $C_{60}$  and other carbon clusters such as  $C_{70}$ ,  $C_{76}$ ,  $C_{78}$  and  $C_{94}$ ...An entirely new branch of chemistry developed with consequences in such diverse areas as astrochemistry, superconductivity and materials chemistry/physics...

27. Thus, in my opinion, there is no reasonable doubt that the above-identified application describes a process for preparing fullerenes, including  $C_{60}$ , in macroscopic amounts and the process described therein provides sufficient detail for an ordinary skilled artisan in 1990 to make the same without an undue amount of experimentation.

28. I have reviewed pages 2-4 of the Office Action issued in the above-identified application and in USSN 486,669. In the Office Action in the above-identified application, the Office Action equates tonnage quantities with the term "macroscopic". It is my opinion that such logic is unjustified, since the skilled artisan would not equate "macroscopic amounts" with tonnage quantity. As defined hereinabove, macroscopic amounts is that amount which can be seen by the naked eye. As explained hereinabove, by following the procedure described in the application, macroscopic amounts of fullerenes, including  $C_{60}$ , are obtained. In fact, gram quantities are routinely available by the Kratschmer and

Huffman method described in the above-identified application, which amounts are in macroscopic amounts in accordance with the standard use of that term. Moreover, it is my opinion that the embodiment in the above-identified application can be modified without an undue amount of experimentation to produce fullerenes, including  $C_{60}$ , in a continuous process.

29. In USSN 486,669, the Office Action alleges that the application does not describe nor provide sufficient information to permit one skilled in the art to easily produce caged carbon molecules consisting solely of carbon atoms which are soluble in non-polar organic solvents. I disagree absolutely and totally. In my opinion, the term "caged carbon molecules consisting solely of carbon atoms which are soluble in non-polar organic solvents" uniquely describes fullerenes, and as indicated hereinabove, it is my opinion that the application describes the preparation of macroscopic amounts of fullerenes.

30. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both under section 1001 of Title 18 of the United States Code and that such willful false statements

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may jeopardize the validity of the application or any patent  
issued thereon.

16<sup>th</sup> November 1999  
DATE

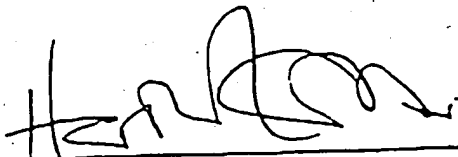
  
HAROLD W. KROTO, PH.D.

Exhibit 1

## CURRICULUM VITAE I

Professor Sir Harold Kroto FRS, Royal Society Research Professor

The School of Chemistry, Physics and Environmental Science,  
The University of Sussex, Brighton, BN1 9QJ, UK

Tel 01 273 678329 desk  
01 273 606755 Univ  
Fax 01 273 677196 dept  
email kroto@sussex.ac.uk

Born 7th Oct 1939 Wisbech, Cambridgeshire, England.

### Education

1947-58 Bolton School, Bolton, Lancashire.  
1958-61 BSc, Sheffield, 1st class honours degree (Chemistry)  
1961-64 PhD, Sheffield, *Electronic Spectroscopy of Unstable Molecules*; Supervisor: R N Dixon  
1964-65 PDF, NRC (Ottawa) with D A Ramsay  
1965-66 PDF, NRC (Ottawa) with C C Costain  
1966-67 Memb. Tech. Staff, Bell Laboratories, Murray Hill, NJ (with Y H Pao, and D P Santry)

### University Career (University of Sussex 1967-)

1967-68 (Tutorial Fellow); 1968-78 (Lecturer); 1978-85 (Reader)  
1985-91 (Professor); 1991- (Royal Society Research Professor)

### Awards

1981-82 Tilden Lecturer (Royal Society of Chemistry)  
1990 Elected Fellow of the Royal Society  
1991- Royal Society Research Professorship  
1992 International Prize for New Materials  
(American Physical Society/IBM, with R F Curl and R E Smalley)  
Italgas Prize for Innovation in Chemistry  
Université Libre de Bruxelles (DHC)  
University of Stockholm (PhDHC)  
Longstaff Medal 1993 (Royal Society of Chemistry)  
Academia Europaea (Member)  
1993 University of Limburg (DHC)  
1994 Hewlett Packard Europhysics Prize  
(with D R Huffman, W Krätschmer and R E Smalley)  
Moët Hennessy® Louis Vuitton Science pour l'Art Prize  
1995 University of Sheffield (Hon Degree)  
University of Kingston (Hon Degree)  
1996 Knighthood, Nobel Prize for Chemistry (with R F Curl and R E Smalley)  
1997 University of Sussex (Hon Degree)  
University of Helsinki (DHC)

### Extra-university administration

SRC Millimetre Wave Telescope Sub-Committee 1977-81  
SERC Millimetre Wave Telescope Users' Committee 1981-85  
SERC Physical Chemistry Subcommittee 1987-90  
SERC Synchrotron Radiation Facility Committee 1987-90  
SERC Chemistry Committee 1988-91  
IAU Sub-group on Astrophysical Chemistry 1987-  
MBI Advisory Board of the Max Born Institute (Berlin) 1993-

## RESEARCH

### Main research areas:

- I Spectroscopy of Unstable Species and Reaction Intermediates  
(Infrared, Photoelectron, Microwave and Mass Spectrometry)
- II Cluster Science  
(Carbon and Metal Clusters, Microparticles, Nanofibres)
- III Fullerenes  
(Chemistry, Physics and Materials Science)
- IV Astrophysics  
(Interstellar Molecules and Circumstellar Dust)

### Research Highlights:

- a) Synthesis in 1976 of the first phosphalkenes (compounds containing the free carbon phosphorus double bond) in particular  $\text{CH}_2=\text{PH}$  (with N P C Simmons and J F Nixon, Sussex), Refs 1,7.
- b) Synthesis in 1976 of the first analogues of HCP, the phosphalkynes which contain the carbon phosphorus triple bond - in particular  $\text{CH}_3\text{CP}$  (with N P C Simmons and J F Nixon, Sussex), Refs 2,7.
- c) The discovery (1976-8) of the cyanopolyynes,  $\text{HC}_n\text{N}$  ( $n=5,7,9$ ), in interstellar space (with D R M Walton A J Alexander and C Kirby (Sussex) and T Oka, L W Avery, N W Broten and J M MacLeod (NRC Ottawa)), Ref 4-6, based on microwave measurements made at Sussex, Refs 3,7.
- d) The discovery of  $\text{C}_{60}$ : Buckminsterfullerene in 1985 (with J R Heath, S C O'Brien, R F Curl and R E Smalley), Refs 8,13,15.
- e) The detection of endohedral metallofullerene complexes (with J R Heath, S C O'Brien, Q Zhang, Y Liu, R F Curl, F K Tittel and R E Smalley), Ref 9
- f) The prediction that  $\text{C}_{60}$  should be produced in combustion processes and might indicate how soot is formed (with Q L Zhang, S C O'Brien, J R Heath, Y Liu, R F Curl and R E Smalley) Ref 10
- g) The explanation of why  $\text{C}_{70}$  is the second stable fullerene (after  $\text{C}_{60}$ ) and the discovery of the *Pentagon Isolation Rule* as a criterion for fullerene stability in general (Refs 11,13,15)
- h) The prediction of the tetrahedral structure of  $\text{C}_{28}$  and the possible stability of "tetravalent" derivatives such as  $\text{C}_{28}\text{H}_4$  Refs 11,15.
- i) The prediction that giant fullerenes have quasi-icosahedral shapes and the detailed structure of concentric shell graphite microparticles (with K G McKay), Refs 12,13.
- j) The mass spectrometric identification and solvent extraction (with J P Hare and A Abdul-Sada) of  $\text{C}_{60}$  from arc processed carbon in 1990 - independently from and simultaneously with the Heidelberg/Tucson group; Refs 14,15.
- k) The chromatographic separation/purification of  $\text{C}_{60}$  and  $\text{C}_{70}$  and  $^{13}\text{C}$  NMR measurements which provided unequivocal proof that these species had fullerene cage structures (with J P Hare and R Taylor, Sussex), Refs 14,15.



#### Meetings (director, organiser or co-organiser)

Brioni International Conferences 1988, 1990, 1993, ...  
Royal Society Discussion Meeting 1992  
Fullerene Symposium 1993 (Santa Barbara)  
Cursos de Verano (El Escorial) *Fullerenos* 1994

#### Editorial Boards

*Chemical Society Reviews* 1986- (Chairman 1990-)  
*Zeitschrift für Physik D* (Atoms Molecules and Clusters) 1992-  
*Carbon* (1992-)  
*J. Chem. Soc. Chem. Comm.* (1993-)

#### Research Details

##### *University of Sheffield*

1961-64      PhD in Free radical spectroscopy by flash photolysis

##### *National Research Council*

1964-65      Free radical spectroscopy by flash photolysis  
1965-66      Microwave Spectroscopy

##### *Bell Telephone Laboratories*

1966-67      Raman Spectroscopy of Liquids, Quantum Chemistry

##### *University of Sussex*

1967-72      Free radical spectroscopy/flash photolysis  
1967-73      Liquid phase interactions/Raman Spectroscopy  
1970-      Unstable species/Microwave Spectroscopy  
1972-90      Unstable species/Photoelectron Spectroscopy  
1976-      Interstellar Molecules/Radioastronomy  
1983-90      Unstable species/Fourier Transform IR Spectroscopy  
1985-      Cluster Studies/Carbon, Metals  
1990-      Fullerene Chemistry, Carbon nanostructures

#### Temporary Appointments (Visiting Professorships etc)

1974      Visiting Associate Professor, UBC Vancouver (3 months)  
1976      Visiting Scientist, NRC Ottawa (3 wks)  
1978      Visiting Scientist, NRC Ottawa (3 wks)  
1981      Visiting Professor, USC (3 months).  
1983      British Council Visitor, Inst Rudjer Boskovic (Zagreb)  
1987      CNRS (1 month) Univ Paris Sud (Orsay)  
1988-      Visiting Professor UCLA (Astronomy)  
1996      Senior Visiting Research Fellow (UC Santa Barbara)

#### Extramural Activities

##### *Sport*

Tennis and Squash for Sheffield University (1959-1964).  
University Athletics Union Finalists - Tennis (1962 and 1963)  
President of Athletics Council, Sheffield University (1963-64)

##### *Television Film*

Chairman of Board of *VEGA SCIENCE TRUST*  
Executive producer of seven 1-hour Television Films of Royal Institution Discourses for Vega/BBCFocus

##### *Graphic Art and Design*

Art Editor *Arrows* Sheffield University Arts Magazine 1962-64

## PUBLICATIONS

240 research papers; book "*Molecular Rotation Spectra*" (Wiley 1975 - reprinted with a new preface Dover 1992)

### Key Publications

- 1) M J Hopkinson, H W Kroto, J F Nixon and N P C Simmons, 'The detection of unstable molecules by microwave spectroscopy: phospho-alkenes  $\text{CF}_2=\text{PH}$ ,  $\text{CH}_2=\text{PCl}$  and  $\text{CH}_2=\text{PH}$ ', *J.C.S. Chem. Comm.*, 513-515 (1976).
- 2) M J Hopkinson, H W Kroto, J F Nixon and N P C Simmons, 'The detection of the reactive molecule 1-phosphapropyne,  $\text{CH}_3\text{CP}$ , by microwave spectroscopy', *Chem. Phys. Letts.*, 42, 460-461 (1976).
- 3) A J Alexander, H W Kroto and D R M Walton, 'The microwave spectrum, substitution structure and dipole moment of cyanobutadiyne,  $\text{HC}_5\text{N}$ ', *J. Mol. Spectrosc.*, 62, 175-180 (1976).
- 4) L W Avery, N W Broten, J M MacLeod, T Oka and H W Kroto, 'Detection of the heavy interstellar molecule cyanodiacetylene', *Astrophys. J.*, 205, L173-175 (1976).
- 5) H W Kroto, C Kirby, D R M Walton, L W Avery, N W Broten, J M MacLeod and T Oka, 'The Detection of Cyanoheptatriyne,  $\text{HC}_7\text{CN}$ , in Heiles' Cloud 2', *Astrophysics J.*, 219, L133-L137 (1978).
- 6) N W Broten, T Oka, L W Avery, J M MacLeod and H W Kroto, 'The Detection of  $\text{HC}_9\text{N}$  in Interstellar Space', *Astrophys. J.*, 223, L105-107 (1978).
- 7) H W Kroto, 'Semistable Molecules in the Laboratory and in Space', Royal Society of Chemistry Tilden Lecture; *Chem. Soc. Revs.*, 11, 435-491 (1982).
- 8) H W Kroto, J R Heath, S C O'Brien, R F Curl and R E Smalley, ' $\text{C}_{60}$ : Buckminsterfullerene', *Nature*, 318(No.6042), 162-163, (1985)
- 9) J R Heath, S C O'Brien, Q Zhang, Y Liu, R F Curl, H W Kroto, F K Tittel and R E Smalley 'Lanthanum Complexes of Spheroidal Carbon Shells', *J. Am. Chem. Soc.*, 107, 7779-7780 (1985).
- 10) Q L Zhang, S C O'Brien, J R Heath, Y Liu, R F Curl, H W Kroto and R E Smalley. 'Reactivity of large carbon clusters Spheroidal Carbon Shells and their possible relevance to the formation and morphology of soot', *J. Phys. Chem.*, 90, 525-528 (1986)
- 11) H W Kroto, 'The Stability of the Fullerenes  $\text{C}_n$  ( $n = 24, 28, 32, 50, 60$  and  $70$ )', *Nature* 329, 529-531 (1987)
- 12) H W Kroto and K McKay, 'The Formation of Quasi-icosahedral Spiral Shell Carbon Particles' *Nature*, 331, 328-331 (1988)
- 13) H W Kroto "Space, Stars,  $\text{C}_{60}$  and Soot", *Science*, 242, 1139-1145 (1988)
- 14) R Taylor, J P Hare, A K Abdul-Sada, and H W Kroto, "Isolation, Separation and Characterisation of the Fullerenes  $\text{C}_{60}$  and  $\text{C}_{70}$ : The Third Form of Carbon." *J. Chem. Soc. Chem. Commun.*, 1423-1425 (1990)
- 15) H W Kroto " $\text{C}_{60}$ : Buckminsterfullerene, the Celestial Sphere that Fell to Earth", *Angewandte Chemie* 31, 111-129 (1992)

Winner of *Sunday Times* Book Jacket Design Competition 1963

Editor, design and layout of *Chemistry at Sussex*

Cover design featured in *Modern Publicity* 1979 (international annual of Graphic Design)

Publicity and logos for Chemical Society Meetings

Logo, letterheads for Science and Engineering at Sussex

Publicity, logo, letterheads, poster for BA Meeting 1983

New Scientist BA Advertisement

Logo and letterhead for Inorganic Biochemistry Discussion Group

Logo and letterhead 1990 for *Venture Research International*

(Formerly *BP Venture Research*)

New Cover design and layout for *Chemical Society Reviews*

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*Sybil P. Parker  
Editor in Chief*

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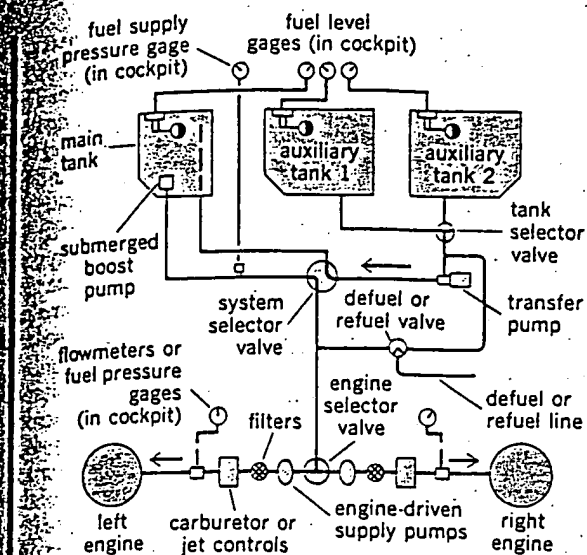


Diagram of a typical aircraft fuel system.

is usually such that all the fuel supply will pass to the engines by way of the main tank, which is refilled as necessary from the auxiliary tanks. In case of emergency, the system selector valve may connect the auxiliary tanks to the engines directly. (F.C.M./J.A.B.)

**Fugacity** A function introduced by G. N. Lewis to facilitate the application of thermodynamics to real systems. Thus, when fugacities are substituted for partial pressures in the mass action equilibrium constant expression, which applies strictly only to the ideal case, a true equilibrium constant results for real systems as well.

The fugacity  $f_i$  of a constituent  $i$  of a thermodynamic system is defined by the following equation (where  $\mu_i$  is the chemical

$$\mu_i = \mu_i^* + RT \ln f_i$$

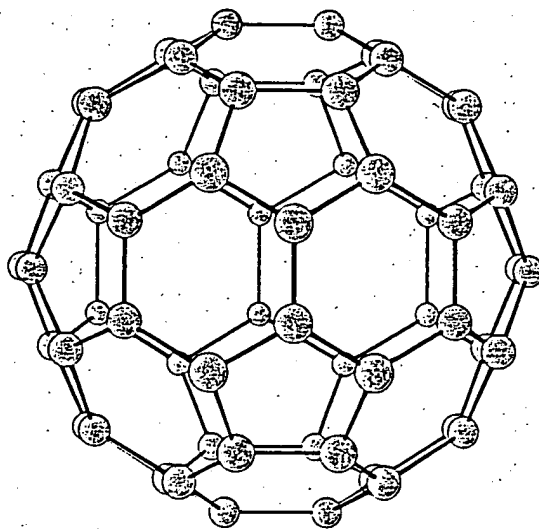
potential and  $\mu_i^*$  is a function of temperature only), in combination with the requirement that the fugacity approach the partial pressure as the total pressure of the gas phase approaches zero. At a given temperature, this is possible only for a particular value for  $\mu_i^*$ , which may be shown to correspond to the chemical potential the constituent would have as the pure gas in the ideal gas state at 1 atm pressure. This definition makes the fugacity identical to the partial pressure in the ideal gas case. For real gases, the ratio of fugacity to partial pressure, called the fugacity coefficient, will be close to unity for moderate temperatures and pressures. At low temperatures and appropriate pressures, it may be as small as 0.2 or less, whereas at high pressures at any temperature it can become very large. See ACTIVITY (THERMODYNAMICS); CHEMICAL EQUILIBRIUM; CHEMICAL THERMODYNAMICS; GAS. (P.J.B.)

**Fullerene** A molecule containing an even number of carbon atoms arranged in a closed hollow cage. The fullerenes were discovered as a consequence of astrophysically motivated chemical physics experiments that were interpreted by using geodesic architectural concepts. Fullerene chemistry, a new field that appears to hold much promise for materials development and other applied areas, was born from pure fundamental science. See CARBON.

In 1985, fifteen years after it was conceived theoretically, the molecule buckminsterfullerene ( $C_{60}$  or fullerene-60) was discovered serendipitously. Fullerene-60 (see illustration) is the archetypal member of the fullerenes, a set of hollow, closed-cage molecules consisting purely of carbon. The fullerenes can be considered, after graphite and diamond, to be the third well-defined allotrope of carbon.

In the fullerene molecule an even number of carbon atoms are arrayed over the surface of a closed hollow cage. Each atom is trigonally linked to its three near neighbors by bonds that delineate a polyhedral network, consisting of 12 pentagons and  $n$  hexagons. All 60 atoms in fullerene-60 are equivalent and lie on the surface of a sphere distributed with the symmetry of a truncated icosahedron. The 12 pentagons are isolated and interspersed symmetrically among 20 linked hexagons; that is, the symmetry is that of a modern soccerball. The molecule was named after R. Buckminster Fuller, the inventor of geodesic domes, which conform to the same underlying structural formula. Three of the four valence electrons of each carbon atom are involved in the  $sp^2$  sigma-bonding skeleton, and the fourth  $p$  electron is one of 60 involved in a pi-delocalized molecular-orbital electron sea that covers the outside (exo) and inside (endo) surface of the molecule. The resulting cloud of pi electron density is similar to that which covers the surface of graphite; indeed, the molecule can be considered a round form of graphite. See ELECTRON CONFIGURATION; GRAPHITE.

Fullerene-60 behaves as a soft electrophile, a molecule that readily accepts electrons during a primary reaction step. It can accept three electrons readily and perhaps even more. The molecule can be multiply hydrogenated, methylated, ammonated, and fluorinated. It forms exohedral complexes in which an atom (or group) is attached to the outside of the cage, as well as endohedral complexes in which an atom (for example, lanthanum (La), potassium (K), or calcium (Ca)) is trapped inside the cage.

Structure of  $C_{60}$  (buckminsterfullerene).

Fullerene materials have been available for such a short time that applications are yet to be established. However, the properties already discovered suggest that there is likely to be a wide range of areas in which the fullerenes or their derivatives will have uses.

Fullerene-60 was discovered as a direct result of physicochemical investigations that simulated processes occurring in stars and in space. Consequently the likelihood that fullerenes, in particular fullerene-60, and analogs are present in space is a fascinating conjecture. (H.W.K.)

**Fuller's earth** Any natural earthy material (such as clay materials) which decolorizes mineral or vegetable oils to a sufficient extent to be of economic importance. It has no mineralogic significance. The clay minerals present in fuller's earth may include montmorillonite, attapulgite, and kaolinite.

# nature

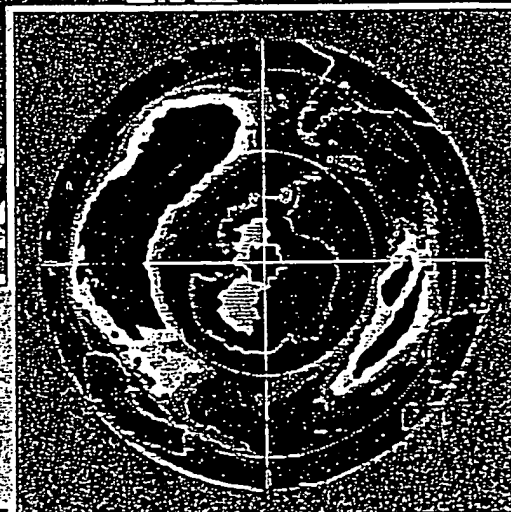
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**A NEW FORM  
OF CARBON**

**UNDERSTANDING ANTARCTIC  
OZONE DEPLETION**



**The cellular defect behind cystic fibrosis**

# Solid C<sub>60</sub>: a new form of carbon

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A new form of pure, solid carbon has been synthesized consisting of a somewhat disordered hexagonal close packing of soccer-ball-shaped C<sub>60</sub> molecules. Infrared spectra and X-ray diffraction studies of the molecular packing confirm that the molecules have the anticipated 'fullerene' structure. Mass spectroscopy shows that the C<sub>70</sub> molecule is present at levels of a few per cent. The solid-state and molecular properties of C<sub>60</sub> and its possible role in interstellar space can now be studied in detail.

FOLLOWING the observation that even-numbered clusters of carbon atoms in the range C<sub>30</sub>-C<sub>100</sub> are present in carbon vapour<sup>1</sup>, conditions were found<sup>2-4</sup> for which the C<sub>60</sub> molecule could be made dominant in the large-mass fraction of vapourized graphite. To explain the stability of the molecule, a model was proposed of an elegant structure in which the carbon atoms are arranged at the 60 vertices of a truncated icosahedron, typified by a soccer ball. The structure, dubbed buckminsterfullerene<sup>2</sup> because of its geodesic nature, has been the subject of several theoretical stability tests<sup>5,6</sup> and has been discussed widely in the literature. Calculations of many physical properties have been made, including electron energies<sup>7-9</sup>, the optical spectrum<sup>9</sup>, vibrational modes<sup>10-15</sup>, and the electric and magnetic properties<sup>16,17</sup>. There has been speculation on the possible chemical and industrial uses of C<sub>60</sub> (ref. 2), and on its importance in astrophysical environments<sup>18-20</sup>. Until now, it has not been possible to produce sufficient quantities of the material to permit measurement of the physical properties, to test the theoretical calculations, or to evaluate the possible applications.

Some of us have recently reported evidence<sup>21,22</sup> for the presence of the C<sub>60</sub> molecule in soot condensed from evaporated graphite. The identification was based primarily on the observed isotope shifts of the infrared absorptions when <sup>12</sup>C was replaced by <sup>13</sup>C, and on comparison of the observed features with theoretical predictions. The measured infrared and ultraviolet absorption bands were superimposed on a rather large continuum background absorption from the graphitic carbon which comprised ≥95% of the sample. Here we report how to extract the carrier of the features from the soot, how to purify it, and evidence that the material obtained is in fact primarily C<sub>60</sub>.

## Method of production

The starting material for our process is pure graphitic carbon soot (referred to below as simply soot) with a few per cent by weight of C<sub>60</sub> molecules, as described in refs 21, 22. It is produced by evaporating graphite electrodes in an atmosphere of ~100 torr of helium. The resulting black soot is gently scraped from the collecting surfaces inside the evaporation chamber and dispersed in benzene. The material giving rise to the spectral features attributed to C<sub>60</sub> dissolves to produce a wine-red to brown liquid, depending on the concentration. The liquid is then separated from the soot and dried using gentle heat, leaving a residue of dark brown to black crystalline material. Other non-polar solvents, such as carbon disulphide and carbon tetrachloride, can also dissolve the material. An alternative con-

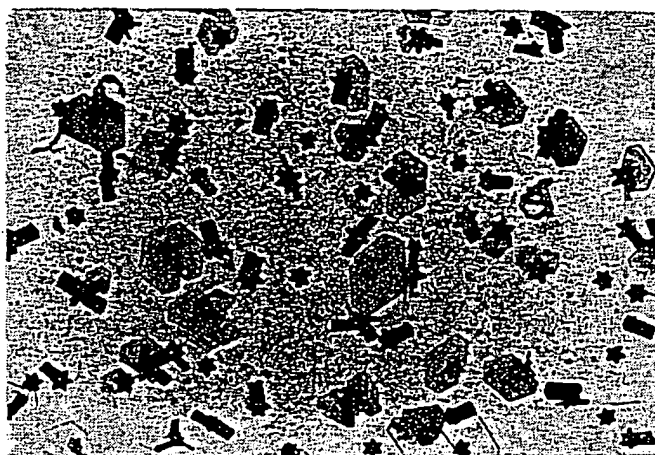


FIG. 1 Transmission micrograph of typical crystals of the C<sub>60</sub> showing thin platelets, rods and stars of hexagonal symmetry.

centration procedure is to heat the soot to 400 °C in a vacuum or in an inert atmosphere, thus subliming the C<sub>60</sub> out of the soot (W. Schmidt, personal communication). The sublimed coatings are brown to grey, depending on the thickness. The refractive index in the near-infrared and visible is about two. To purify the material, we recommend removing the ubiquitous hydrocarbons before the concentration procedure is applied (for example, by washing the initial soot with ether). Thin films and powder samples of the new material can be handled without special precautions and seem to be stable in air for at least several weeks, although there does seem to be some deterioration with time for reasons that are as yet unclear. The material can be sublimed repeatedly without decomposition. Using the apparatus described, one person can produce of the order of 100 mg of the purified material in a day.

Studies by optical microscopy of the material left after evaporating the benzene show a variety of what appear to be crystals—mainly rods, platelets and star-like flakes. Figure 1 shows a micrograph of such an assemblage. All crystals tend to exhibit six-fold symmetry. In transmitted light they appear red to brown in colour; in reflected light the larger crystals have a metallic appearance whereas the platelets show interference colours. The platelets can be rather thin and are thus ideally suited for electron-diffraction studies in an electron microscope (see the inset in Fig. 3).

## Mass spectroscopy

The material has been analysed by mass spectrometry at several facilities. All mass spectra have a strong peak at mass 720 a.m.u., the mass of C<sub>60</sub>. Significant differences in the spectra occur only at masses lower than 300 a.m.u. Most of these differences seem to originate from the different ionization techniques and in the different methods of desorbing molecules from the sample. Mass spectra recorded at low and high resolution are shown in Fig. 2. The spectra were obtained using a time-of-flight secondary-ion mass spectrometer<sup>23</sup> and a C<sub>60</sub>-coated stainless-steel plate. In the mass range above 300 a.m.u., the spectrum is dominated by C<sub>60</sub> ions and its fragments (even-numbered clusters of atomic carbon), and C<sub>70</sub> ions. In this sample, the ratio of C<sub>70</sub> to C<sub>60</sub> is



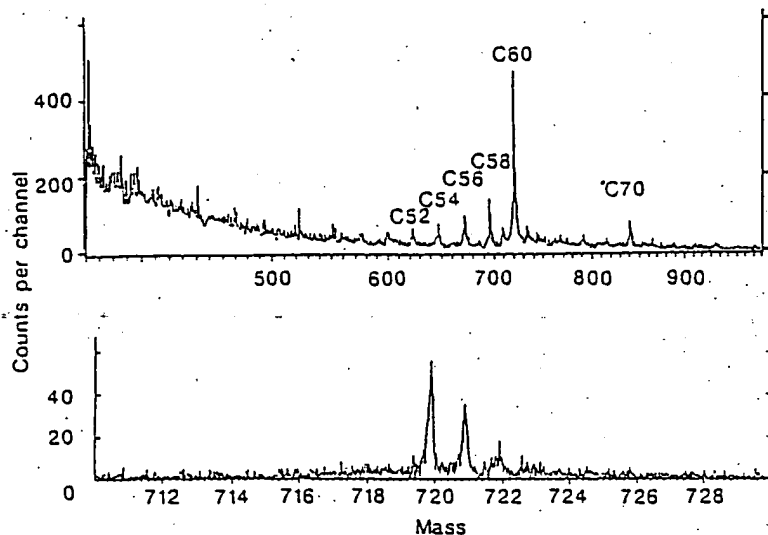


FIG. 2 Low-resolution (top) and high-resolution time-of-flight mass spectra of positive ions obtained from coatings of solid  $C_{60}$ . A 5-keV  $Ar^+$  ion beam was used to sputter and ionize the sample. The isotope pattern (bottom) is approximately that expected for  $C_{60}$  molecules composed of  $^{12}C$  and  $^{13}C$  isotopes of natural abundance.

$\sim 0.1$ . The high-resolution mass spectrum shows approximately the expected isotope pattern for  $C_{60}$ . The increasing background in the low-resolution mass spectrum is not produced by the sample—such backgrounds also occur in blank measurements on uncoated stainless-steel substrates.

So far, the cleanest mass spectra have been obtained when the material was evaporated and ionized in the vapour phase by electrons. In such spectra the low-mass background is substantially reduced and the entire mass spectrum is dominated by  $C_{60}$  ions and its fragments. The ratio of  $C_{70}$  to  $C_{60}$  in these mass spectra is  $\sim 0.02$  and seems to be smaller than that shown in Fig. 2. Both ratios are of the order of those reported from laser-evaporation experiments<sup>2,3</sup>. We assume, as previously suggested<sup>24</sup>, that the  $C_{70}$  molecule also has a closed-cage structure, either elongated<sup>24</sup> or nearly spherical<sup>25</sup>. Further details of the mass spectroscopy of the new material will be published elsewhere.

### Structure

To determine if the  $C_{60}$  molecules form a regular lattice, we performed electron and X-ray diffraction studies on the individual crystals and on the powder. A typical X-ray diffraction pattern of the  $C_{60}$  powder is shown in Fig. 3. To aid in comparing the electron diffraction results with the X-ray results we have inset the electron diffraction pattern in Fig. 3. From the hexagonal array of diffraction spots indexed as shown in the figure, a  $d$  spacing of  $8.7 \text{ \AA}$  was deduced corresponding to the (100) reciprocal lattice vector of a hexagonal lattice. The

most obvious correspondence between the two types of diffraction is between the peak at  $5.01 \text{ \AA}$  of the X-ray pattern and the (110) spot of the electron diffraction pattern, which gives a spacing of  $\sim 5.0 \text{ \AA}$ . Assuming that the  $C_{60}$  molecules are behaving approximately as spheres stacked in a hexagonal close-packed lattice with a  $c/a$  ratio of 1.633,  $d$  spacings can be calculated. The results are shown in Table 1. The values derived from this interpretation are  $a = 10.02 \text{ \AA}$  and  $c = 16.36 \text{ \AA}$ . The nearest-neighbour distance is thus  $10.02 \text{ \AA}$ . For such a crystal structure the density is calculated to be  $1.678 \text{ g cm}^{-3}$ , which is consistent with the value of  $1.65 \pm 0.05 \text{ g cm}^{-3}$  determined by suspending crystal samples in aqueous  $GaCl_3$  solutions of known densities. Although the agreement shown in Table 1 is good, the absence of the characteristically strong (101) diffraction of the hexagonal close-packed structure, and the broad continuum in certain regions suggest that the order is less than perfect. Further, X-ray diffraction patterns from carefully grown crystals up to  $500 \text{ \mu m}$  in size with well developed faces yielded no clear spot pattern (in contrast to the electron diffraction pattern on micrometre-sized crystals). It therefore appears that these larger crystals do not exhibit long-range periodicity in all directions.

A likely explanation for these facts lies in the disordered stacking of the molecules in planes normal to the  $c$  axis. It is well known that the positions taken by spheres in the third layer of stacking determines which of the close-packed structures occurs, the stacking arrangement in a face-centred cubic structure being ABCABC... whereas that in a hexagonal close-

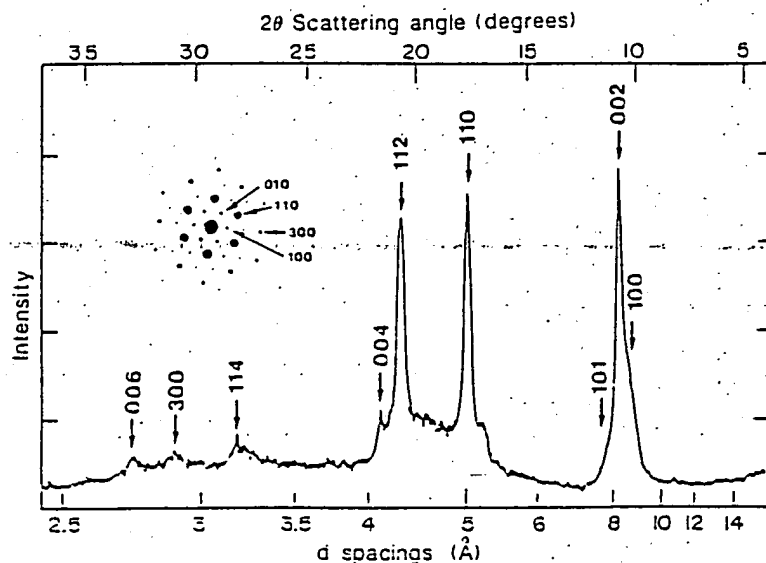


FIG. 3 X-ray diffraction pattern of a microcrystalline powder of  $C_{60}$ . Inset (upper left) is a single-crystal electron diffraction pattern indexed with Miller indices compatible with the X-ray pattern. The pattern is from a thin platelet such as those in Fig. 1 with the electron beam perpendicular to the flat face.

TABLE 1 X-ray diffraction results

Measured 2 $\theta$ (deg)	Measured $d$ spacing (Å)	Calculated $d$ spacing (Å)	Assignment ( $hkl$ )
10.2 shoulder	8.7	8.68	(100)
10.81	8.18	8.18	(002)
		7.68	(101)
17.69	5.01	5.01	(110)
20.73	4.28	4.28	(112)
21.63	4.11	4.09	(004)
28.1	3.18	3.17	(114)
30.8	2.90	2.90	(300)
32.7	2.74	2.73	(006)

Assignments for a hexagonal lattice using  $a=10.02$  Å,  $c=16.36$  Å.  
 $(1/d^2) = \frac{1}{3} [(h^2 + hk + k^2)/a^2] + l^2/c^2$ .

packed structure is ABABAB... If the stacking sequence varies, the X-ray lines owing to certain planes will be broadened by the disorder whereas other lines will remain sharp. Such disordered crystalline behaviour was observed long ago in the hexagonal close-packed structure of cobalt<sup>26-28</sup> where X-ray diffraction lines such as (101), (102) and (202) were found to be substantially broadened by the stacking disorder. Reflections from planes such as (002) remain sharp because these planes have identical spacings in the face-centred cubic and hexagonal close-packed structures. For the planes producing broadened diffraction peaks because of this kind of disorder, the following condition for the Miller indices ( $hkl$ ) has been shown to apply<sup>27,29</sup>:  $h-k=3t\pm1$  (where  $t$  is an integer) and  $l\neq0$ . None of these broadened reflections are apparent in the X-ray pattern of Fig. 3. This may explain the weakness of the characteristically strong (101) peak. Whether or not this stacking disorder is related to the presence of the possibly elongated  $C_{70}$  molecule has yet to be determined.

In small crystals at least, the  $C_{60}$  molecules seem to assemble themselves into a somewhat ordered array as if they are effectively spherical, which is entirely consistent with the hypothesis that they are shaped like soccer balls. The excess between the nearest-neighbour distance (10.02 Å) and the diameter calculated for the carbon cage itself (7.1 Å) must represent the effective van der Waals diameter set by the repulsion of the  $\pi$  electron clouds extending outward from each carbon atom. Because the van der Waals diameter of carbon is usually considered to be 3.3–3.4 Å the packing seems a little tighter than one might expect for soccer-ball-shaped  $C_{60}$  molecules. The reason for this has not yet been determined.

In summary, our diffraction data imply that the substance isolated is at least partially crystalline. The inferred lattice constants, when interpreted in terms of close-packed icosahedral  $C_{60}$ , yield a density consistent with the measured value. Further evidence that the molecules are indeed buckminsterfullerene and that the solid primarily consists of these molecules comes from the spectroscopic results.

### Spectroscopy

The absorption spectra of the graphitic soot<sup>21,22</sup> showed evidence for the presence of  $C_{60}$  in macroscopic quantities. Following the purification steps described above the material can be studied spectroscopically with the assurance that the spectra are dominated by  $C_{60}$ , with some possible effects from  $C_{70}$ . Samples were prepared for spectroscopy by subliming pure material onto transparent substrates for transmission measurements. Depending on the pressure of helium in the sublimation chamber, the nature of the coatings can range from uniform films (at high vacuum) to coatings of  $C_{60}$  smoke (sub-micrometre microcrystalline particles of solid  $C_{60}$ ) with the particle size depending to some extent on the pressure.

Figure 4 shows the transmission spectrum of an  $\sim 2$ - $\mu$ m-thick  $C_{60}$  coating on a silicon substrate. The infrared bands are at the same positions as previously reported<sup>21,22</sup>, with the four most

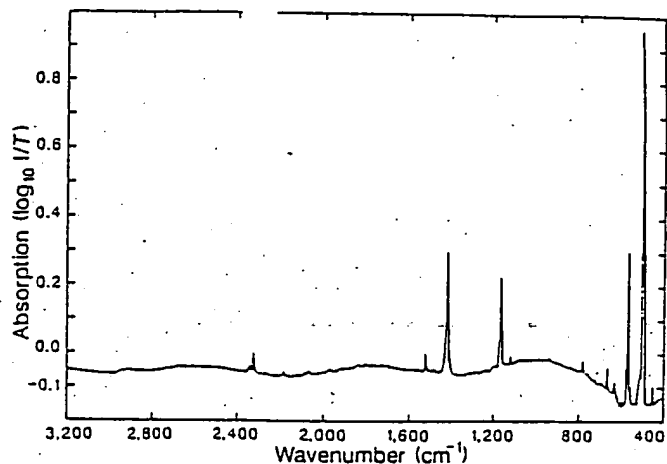


FIG. 4 Infrared absorption spectrum of a coating,  $\sim 2$   $\mu$ m thick, of solid  $C_{60}$  on a silicon substrate, referenced to a clean silicon substrate. Apparent negative absorptions are due to the coating acting in part as a non-reflecting layer.

intense lines at 1429, 1183, 577 and 528  $\text{cm}^{-1}$ ; here, however, there is no underlying continuum remaining from the soot. In many of our early attempts to obtain pure  $C_{60}$ , there was a strong band in the vicinity of 3.0  $\mu$ m, which is characteristic of a CH-stretching mode. After much effort this contaminant was successfully removed by washing the soot with ether and using distilled benzene in the extraction. The spectrum in Fig. 4 was obtained when the material cleaned in such a manner was sublimed under vacuum onto the substrate. The spectrum shows very little indication of CH impurities. Vibrational modes to compare with the measured positions of the four strong bands have been calculated by several workers<sup>10-13</sup>. As noted previously, the presence of only four strong bands is expected for the free, truncated icosahedral molecule with its unusually high symmetry. Also present are a number of other weak infrared lines which may be due to other causes, among which may be absorption by the  $C_{70}$  molecule or symmetry-breaking produced (for example) by isotopes other than  $^{12}\text{C}$  in the  $C_{60}$  molecule or by mutual interaction of the  $C_{60}$  molecules in the solid. Weaker features at  $\sim 2,330$  and  $2,190$   $\text{cm}^{-1}$ , located in the vicinity of the free  $\text{CO}_2$  and  $\text{CO}$  stretching modes, may imply some attachment of the  $\text{CO}_2$  or  $\text{CO}$  to a small fraction of the total number of  $C_{60}$  molecules. Another notable feature is the peak at 675  $\text{cm}^{-1}$ , which is weak in the thin-film substrates but almost as strong as the four main features in the crystals. We suspect that this vibrational mode may be of solid state rather than molecular origin.

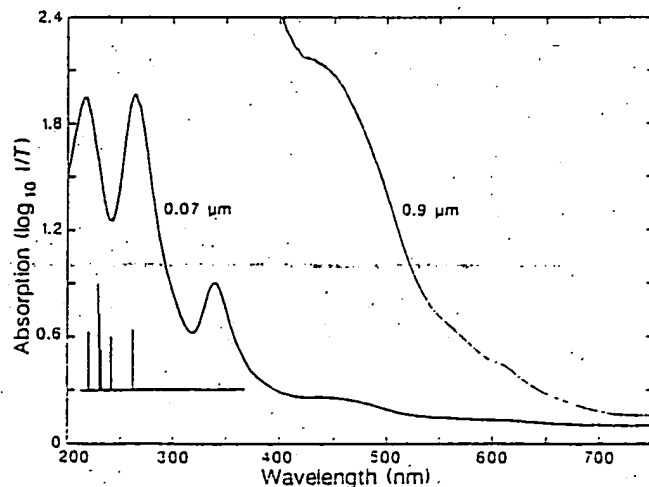


FIG. 5 Visible-ultraviolet absorption spectra of two thicknesses of solid  $C_{60}$  on quartz. The calculated<sup>3</sup> positions and relative oscillator strengths for allowed transitions of  $C_{60}$  are shown on the bottom.

Figure 5 shows an absorption spectrum taken on a uniform film coated on a quartz glass substrate. The ultraviolet features are no longer obscured by the graphitic carbon background as in our previous spectra<sup>22</sup>. Broad peaks at 216, 264 and 339 nm dominate the spectra. Weaker structures show up in the visible, including a plateau between ~460 and 500 nm and a small peak near 625 nm. At the bottom of Fig. 5 we have shown positions and relative oscillator strengths taken from Larsson, Volosov and Rosén<sup>9</sup> calculated for the  $C_{60}$  molecule. They also reported a variety of forbidden bands with the lowest energy ones in the vicinity of 500 nm. There seems to be a rough correspondence between our measurements on solid films and the allowed transitions predicted for the molecule. The possibility exists, however, that one or more of the absorption features shown in Fig. 5 are due to  $C_{70}$ . We still do not observe a band at 386 nm in our films, as observed<sup>30</sup> using a laser depletion spectroscopy method and attributed to the  $C_{60}$  molecule. Quite similar spectra to that in Fig. 5 have been recorded for microcrystalline coatings deposited at helium pressures of 100 torr, for example. The peaks occur at the slightly shifted positions of 219, 268 and 345 nm.

### Possible interstellar dust

The original stimulus for the work<sup>2</sup> that led to the hypothesis of the soccer-ball-shaped  $C_{60}$  molecule, buckminsterfullerene, was an interest in certain unexplained features in the absorption and emission spectra of interstellar matter. These include an intense absorption band at 217 nm which has long been attributed to small particles of graphite<sup>31</sup>, a group of unidentified interstellar absorption bands in the visible that have defied

explanation for more than 70 years<sup>31,32</sup>, and several strong emission bands attributed to polycyclic aromatic hydrocarbons<sup>33,34</sup>. Based on the visible and infrared absorption spectra of Figs 4 and 5, we do not see any obvious matches with the interstellar features. The ultraviolet band at 216–219 nm has a similar peak wavelength to an interstellar feature, although the other strong bands of the spectrum have no interstellar counterparts. As the influence of  $C_{70}$  absorptions on the spectrum is not yet known, a conclusive comparison with the 217-nm interstellar band is difficult. We note that the visible-ultraviolet spectrum presented here is characteristic of a solid, rather than of free molecules. In addition, these new results do not relate directly to absorption in the free- $C_{60}^+$  molecular ion, which has been envisaged<sup>19</sup> to explain the diffuse interstellar bands. Nevertheless, these data should now provide guidance for possible infrared detection of the  $C_{60}$  molecule, if it is indeed as ubiquitous in the cosmos as some have supposed.

### Summary

To our method for producing macroscopic quantities of  $C_{60}$ , we have added a method for concentrating it in pure solid form. Analyses including mass spectroscopy, infrared spectroscopy, electron diffraction and X-ray diffraction leave little doubt that we have produced a solid material that apparently has not been reported previously. We call the solid fullerite as a simple extension of the shortened term fullerene, which has been applied to the large cage-shaped molecules typified by buckminsterfullerene ( $C_{60}$ ). The various physical and chemical properties of  $C_{60}$  can now be measured and speculations concerning its potential uses can be tested. □

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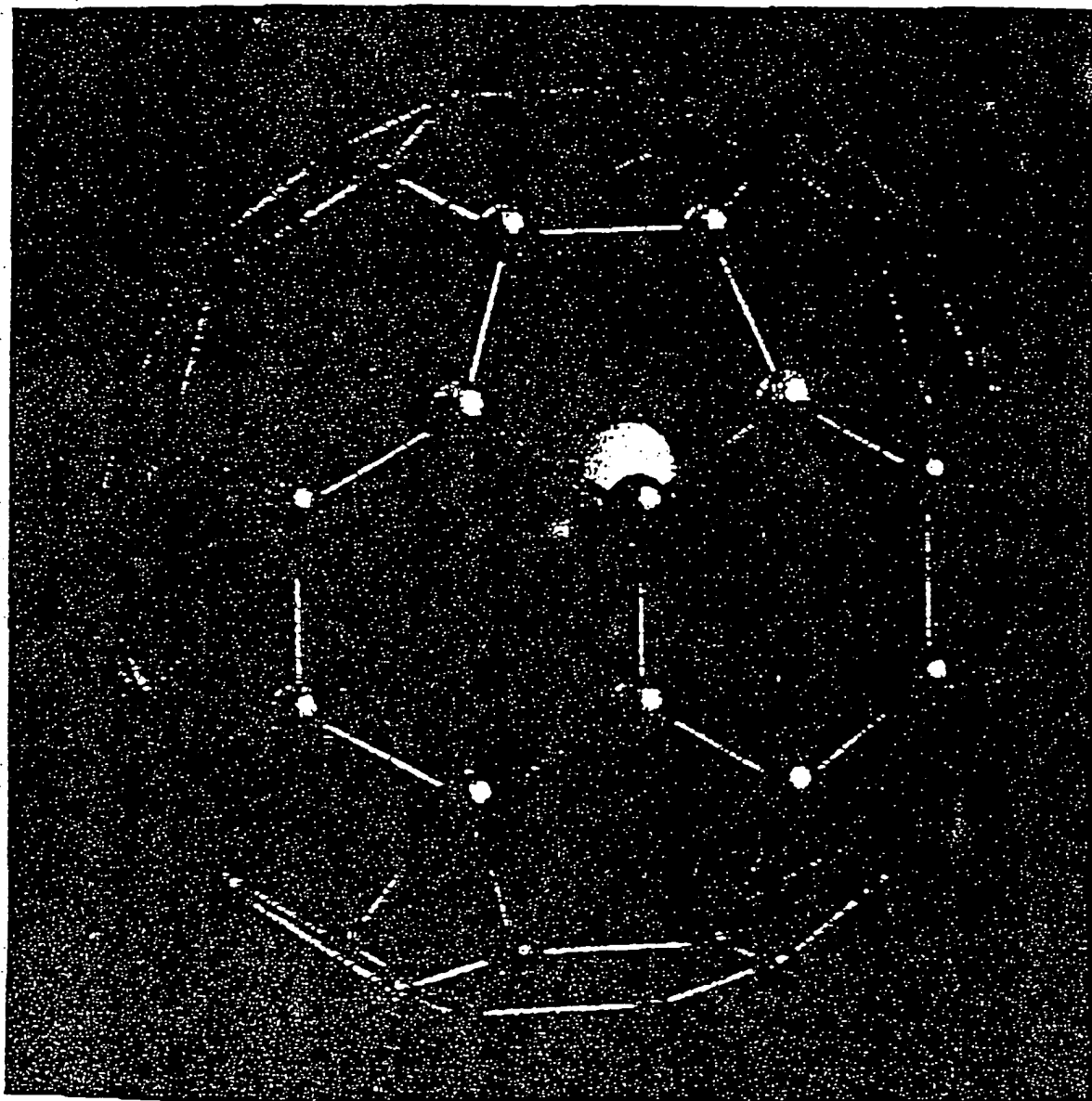
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*Remnants of a planet that failed to form.*

*Still no technological fix for oil spills.*

*What made higher life-forms possible?*



*Buckyball, the third form of pure carbon, cages an atom in its lattice.*

13. Another problem with the methods disclosed in the Buseck et al. article was the use of the laser technique to allegedly detect the  $C_{60}$  and  $C_{70}$  in their sample of shungite. As the skilled artisan is well aware, laser under certain conditions has been used to generate fullerenes. Even though reasonable efforts were made to allay suspicion in this regard, the paper does not entirely eliminate the possibility that  $C_{60}$  and  $C_{70}$  might have been produced during the sampling phase.

14. I also have queries about their findings for other reasons; I would have expected the whole range of related fullerenes to be found with any naturally produced  $C_{60}$  and  $C_{70}$ . Yet, Buseck, et al. did not report any such finding.

15. The Hecht article is a report by a third party, alleging that Dieter Heymann found  $C_{60}$  in New Zealand Clay. However, the article does not present any data or evidence of Heymann in support of the allegations therein.

16. The  $C_{60}$  and  $C_{70}$  described in these articles were allegedly found in trace amounts, in parts per billion. There are no large pockets of fullerenes, e.g.,  $C_{60}$  and  $C_{70}$ , and where they are reported to be found, they are not reported to be found in macroscopic amounts. The amounts of  $C_{60}$  and  $C_{70}$  reportedly found are too small to be useful to the skilled artisan. It does not seem feasible that macroscopic amounts of  $C_{60}$  and  $C_{70}$  will be produced from mining these rocks.

17. Furthermore, when reportedly found in the natural environment, the  $C_{60}$  and  $C_{70}$  are never found as isolates. They are reported to be found as a part of a larger geological sample and are thus very impure.

18. Furthermore, the  $C_{60}$  and  $C_{70}$  reportedly found are alleged to be distributed in a matrix. It is my opinion that crystalline  $C_{60}$  and  $C_{70}$  have not been found in nature.

proposal, published in *Nature* in 1985, had made the quest one of the hottest in chemistry.

In our laboratory we collected the sooty carbon produced by the vaporization laser while using various chemical techniques to detect the presence of  $C_{60}$ . We slurried the soot in benzene, for example, and looked for a yellow color. But the solution in our test tubes stayed clear, with boring black soot sitting on the bottom. The community of cluster chemists ran many more sophisticated experiments but achieved no better result.

Many gave up hope of ever seeing the yellow vial. They reasoned that although the fullerenes may be stable, it was too hard to separate them from the other sooty material being produced in the vaporization experiments. Per-

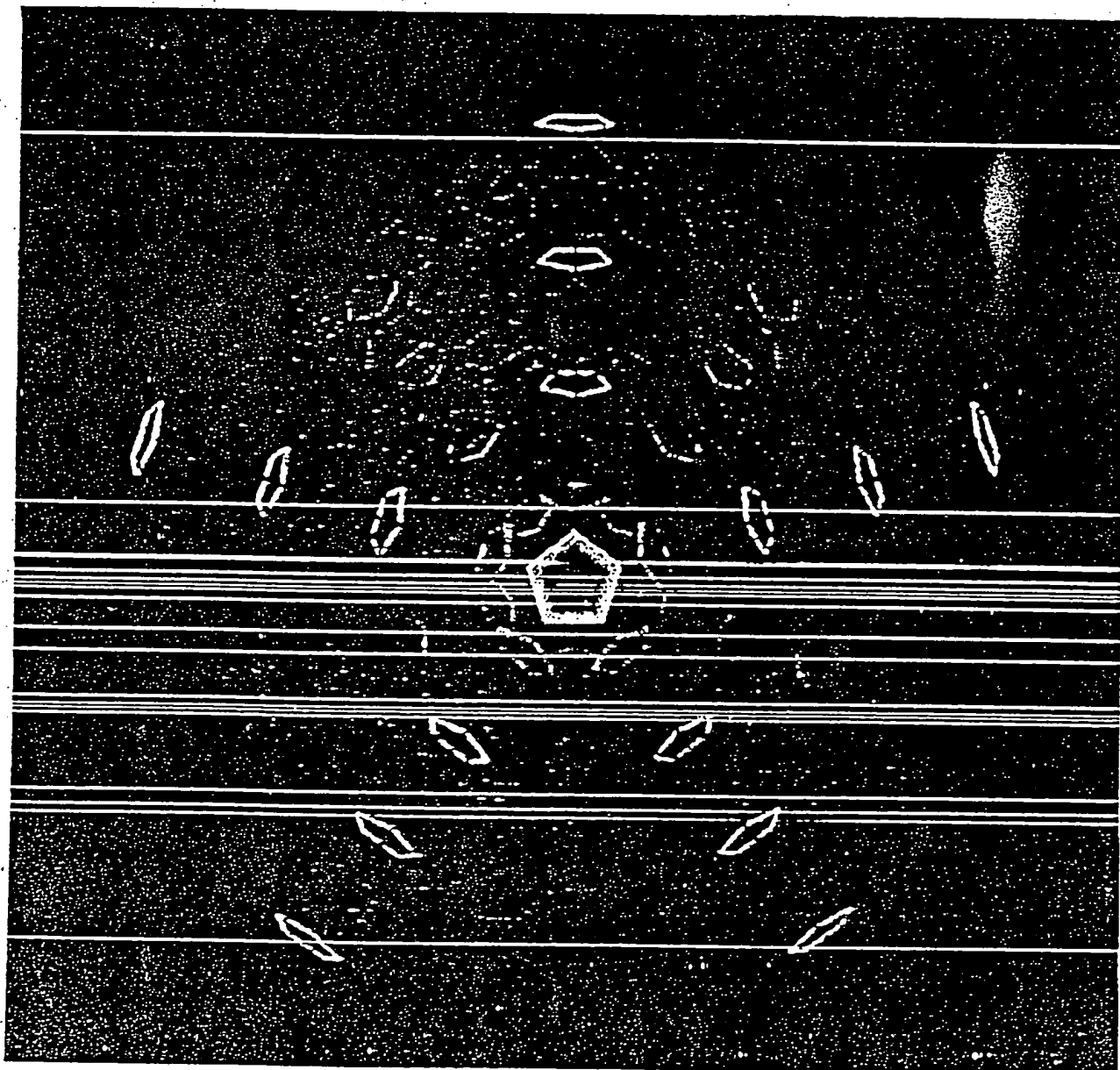
haps, the workers said, some dedicated chemist might one day extract a few micrograms with some special solvent, but no one seriously expected  $C_{60}$  to be available in bulk anytime soon.

In the end, the breakthrough was made not by chemists but by physicists working in a totally different area. Huffman, Krätschmer and their students had been engaged for decades in a study of interstellar dust, which they assumed to consist mainly of particles of carbon (the most common particle-forming element). They therefore modeled the phenomenon in the laboratory by vaporizing carbon and condensing it in as many ways as possible. Optical tests figured in most of the studies. (Virtually all that is known of the interstellar dust stems from obser-

vations of how it absorbs and scatters starlight.)

In 1983 the physicists tried evaporating a graphite rod by resistive heating in an atmosphere of helium. They noticed that when the helium pressure was just right (about a seventh of an atmosphere), the dust strongly absorbed wavelengths in the far ultraviolet region, creating a peculiar, double-humped spectrum [see bottom illustration on page 58]. Most observers would have missed the two blips on the screen, but not Huffman and Krätschmer: they had studied spectra of carbon dust for years without encountering such an effect. They dubbed it their "camel" sample and wondered what it meant.

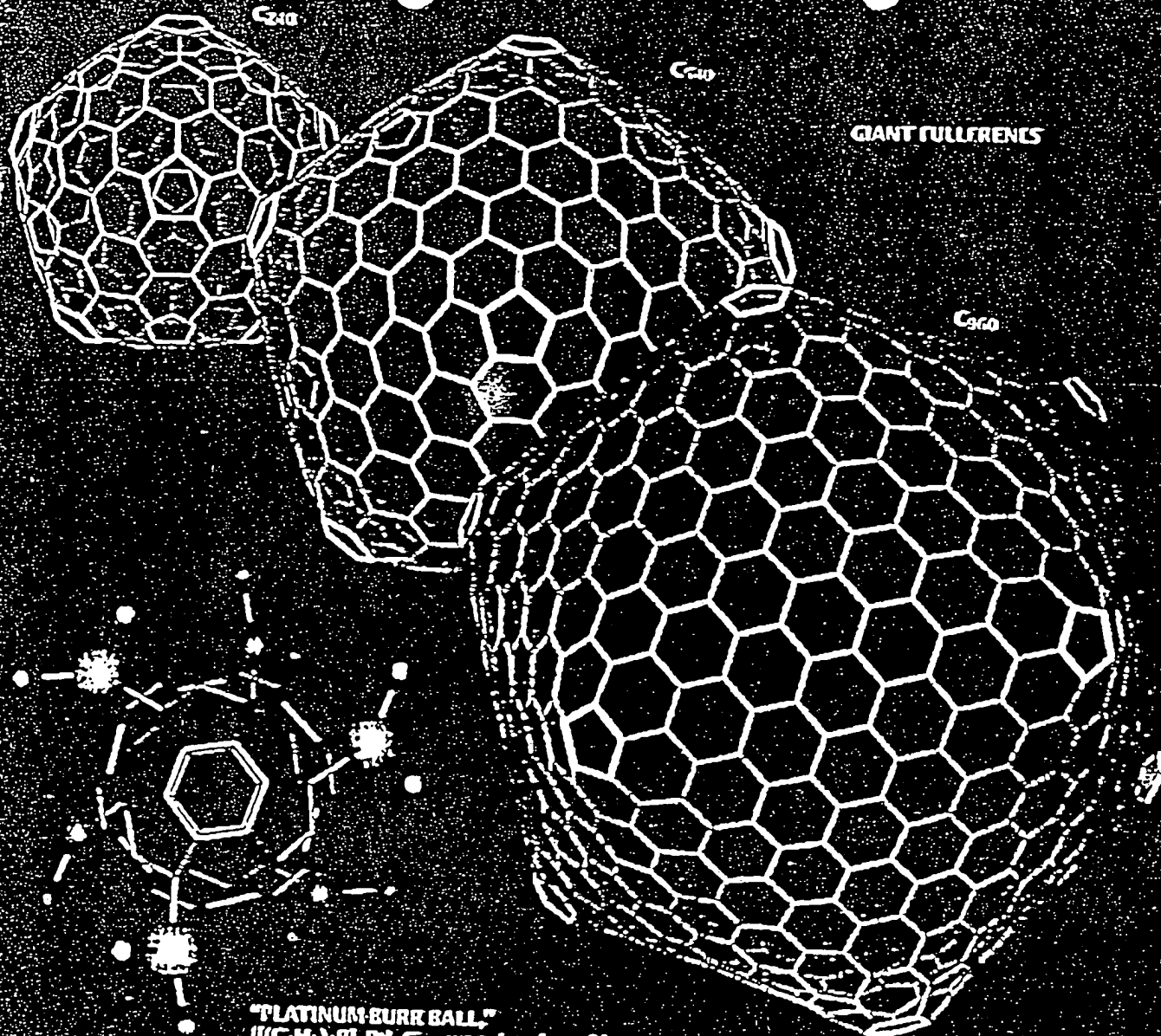
Nearly three years later, in the late fall of 1985, Huffman read in *Nature* of



Influenced by their background in physics, the workers initially chose to test their hypothesis by a rather in-



## GIANT FULLERENES



**"PLATINUM-BURK BALL,"**  
 $[(C_6H_5)_2Pt]_n$ , was developed by  
 Paul J. Fagan and Joseph C. Calabrese  
 of the Central Research and  
 Development Department of Du Pont  
 Company. The  $C_6H_5$  complexes are left  
 out for simplicity's sake.

involved route. They prepared a sample from pure  $^{13}C$ , a heavy isotope of carbon, and verified that the extra mass shifted the four infrared bands in the way expected for so large a molecule composed exclusively of carbon. Ultimately, however, they realized that the simplest assay followed a basic dictum of organic chemistry: like dissolves like. Should their sample dissolve in an aromatic solvent, such as benzene, this would support the predicted aromaticity of  $C_{60}$ . Because benzene molecules take the shape of a ring of carbon at-

oms,  $C_{60}$  would thus be seen as a kind of spherical benzene.

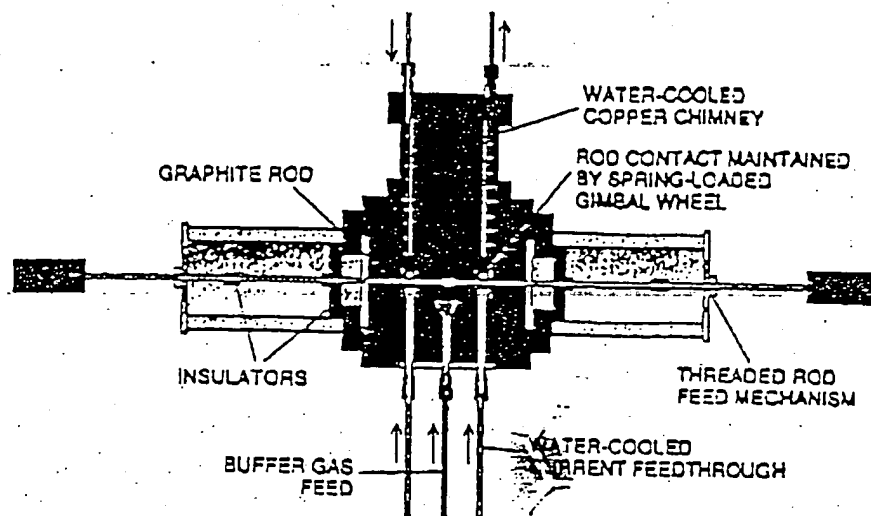
When the Krätschmer-Huffman group finally added benzene to their camel sample and saw the color red develop, they realized they were looking at the first concentrated solution of fullerenes ever seen. They evaporated the solvent and found that tiny crystals remained, which readily redissolved. These crystals could be sublimed under a vacuum near 400 degrees Celsius and condensed on a cold microscope slide to form smooth films of solid materials,

which Krätschmer and Huffman christened "fullerite."

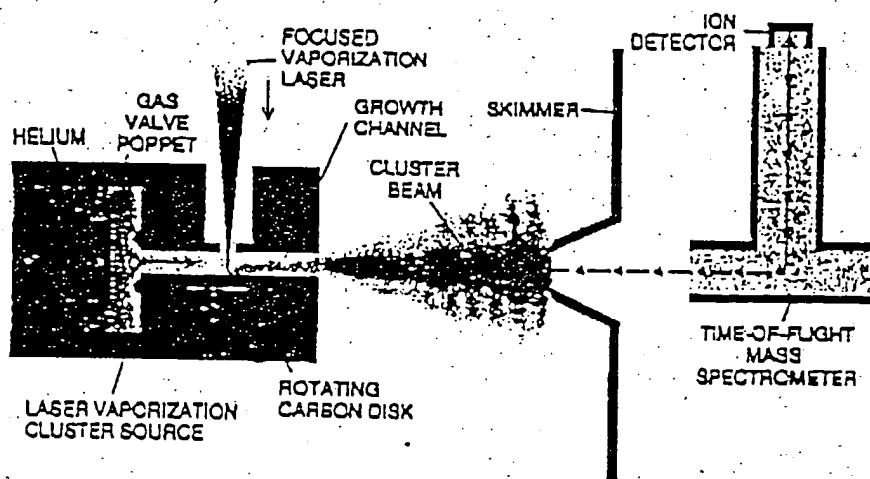
In thin layers these films were yellow (a fact that those of us at Rice University who searched for a "yellow vial" find highly gratifying). Although it took a while to obtain precise numbers, it is now known that carbon dust prepared in the camel way produces an extractable fullerene mixture made up of roughly 75 percent  $C_{60}$  (the soccer ball), 23 percent  $C_{70}$  (the rugby ball) and a grab bag of larger fullerenes.

Here was a new form of pure, solid

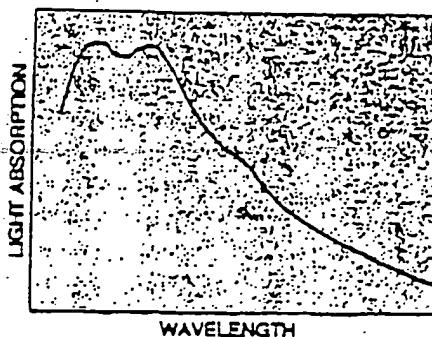
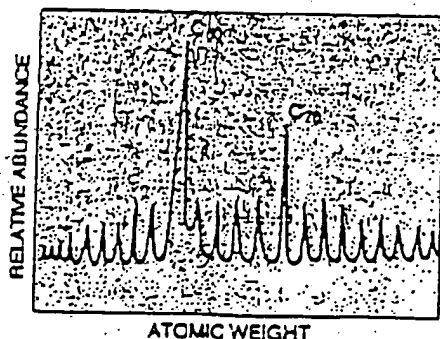




**FULLERENE FACTORY** makes macroscopic samples in a carbon arc. The arc—a refinement of an apparatus developed by Wolfgang Krätschmer and Donald Huffman—frees carbon atoms that coalesce into sheets. Inert helium holds the sheets near the arc long enough for them to close in on themselves, forming fullerenes.



**CLUSTER GENERATOR** designed by one of the authors (Smalley) produced the first evidence that fullerenes can form from carbon vapor. A pulsed laser vaporizes carbon; a gust of helium then sweeps the vapor into a supersonic beam whose expansion cools the atoms, condensing them.



**CRUCIAL GRAPHS:** In 1985 the cluster-beam generator showed many even-numbered carbon clusters, especially  $C_{60}$ , suggesting that these species are particularly stable. The humped ultraviolet absorption spectrum led Krätschmer and Huffman to dub it the "camel" sample; in 1990 it was shown to contain  $C_{60}$ .

carbon. It is the only pure, finite form. The other two, diamond and graphite, are actually infinite network solids. In the real world, one usually deals with lumps of diamond cut out of larger bulk crystals. Under normal conditions, the surfaces of such a piece are instantly covered with hydrogen, which ties up the dangling surface bonds. Graphite is much the same. No piece of diamond, therefore, can ever be truly pure under normal conditions. The fullerenes, on the other hand, need no other atoms to satisfy their chemical bonding requirements on the surface. In this sense, the fullerenes are the first and only stable forms of pure, finite carbon.

Once the Krätschmer-Huffman results were announced at a conference in Konstanz, Germany, in early September 1990, the race was on. The study of  $C_{60}$  and the fullerenes had been the province of the few select groups that had something like our elaborate and expensive laser-vaporization cluster-beam apparatus. Now Krätschmer and Huffman had opened the field to anyone who could procure a thin rod of carbon, a cheap power supply, a bell-jar vacuum chamber and a few valves and gauges. Everybody could play.

Within a few months, many groups were making their own fullerenes. Physicists, chemists and materials scientists thus began an interdisciplinary feeding frenzy that continues to intensify as this article is being written (see box on page 62). The key results have been quickly reproduced in over a dozen laboratories, some of which have applied alternative procedures of verification as well. Because fullerenes are readily soluble and vaporizable molecules that remain stable in air, they are perfectly suited to a wide range of techniques.

One of the most powerful techniques—nuclear magnetic resonance (NMR)—has confirmed the single most critical aspect of the soccerball structure: that all 60 carbon atoms have exactly the same relation to the whole. Only the truncated icosahedral structure we proposed for  $C_{60}$  arranges the atoms so symmetrically as to distribute the strain of closure equally. Such even distribution makes for great strength and stability. Indeed, that is why we proposed the structure in the first place: it explains the extraordinary stability of the 60-atom species.

Because  $C_{60}$  is the most symmetric molecule possible in three-dimensional Euclidean space, it is literally the roundest of round molecules. Edgeless, chargeless and unbound, the molecule spins freely, as NMR experiments show.

more than 100 million times a second. The NMR experiments also dramatically verify that  $C_{70}$  has the shape of a tiny rugby ball: at room temperature, it spins rapidly about its long axis, stopping its frantic motion only below the temperature of liquid air.

High-resolution electron microscopy revealed these little carbon balls one at a time—as predicted, they spanned a bit more than one nanometer (a billionth of a meter). Scanning tunneling microscopy showed that when  $C_{60}$  molecules are deposited on a crystalline surface, they pack as regularly as billiard balls. X-ray diffraction studies demonstrated that—as one would expect— $C_{60}$  crystallizes in a face-centered cubic lattice, with the balls a little more than 10 angstroms apart [see illustration on page 62]. The crystals are as soft as graphite. When squeezed to less than 70 percent of their initial volume, calculations predict that they will become even harder than diamond. When the pressure is relieved, they are observed to spring back to their normal volume. Thrown against steel surfaces at speeds somewhat greater than 17,000 miles per hour (about the orbital speed of the U.S. space shuttle), they are incredibly resilient: they just bounce back.

We found that the most convenient way to generate fullerenes consists of setting up an arc between two graphite electrodes. We maintained a constant gap by screwing the electrodes toward each other as fast as their tips evaporated. The process worked best when the helium pressure was optimized and other gases, such as hydrogen and water vapor, were rigorously eliminated. Such measures produced yields of dissolvable fullerenes that typically ranged between 10 and 20 percent of the vaporized carbon. Yields as high as 45 percent have recently been reported.

The only irreducible cost appears to be that of the electricity needed to run the arc. But even the small bench-top generators we are now using in our laboratory provide electricity at a cost that amounts to only about five cents per gram of  $C_{60}$ . Recently it has been found that a sooting flame (such as that of a candle) can be used to produce substantial yields of  $C_{60}$ . In the long run, this may prove the cheapest way to make the material. When the first large-scale applications of fullerenes are found—perhaps in superconductors, batteries or microelectronics [see box on page 62]—the manufacturing cost of  $C_{60}$  will probably fall close to that of aluminum: a few dollars a pound. What had recently been described as the "most controversial molecule in the

Cosmos" is well on its way to becoming a bulk commodity.

A host of questions arises out of this wonder. What exactly is the helium doing? How can such a perfectly symmetric molecule be formed with such high efficiency out of the chaos of a carbon arc? And, on a more personal level, where did we go wrong? Why did we, and all other chemists for that matter, fall in the search for the yellow vat? Our technique involved helium as well. What did the Krätschmer-Huffman team do that made such a big difference?

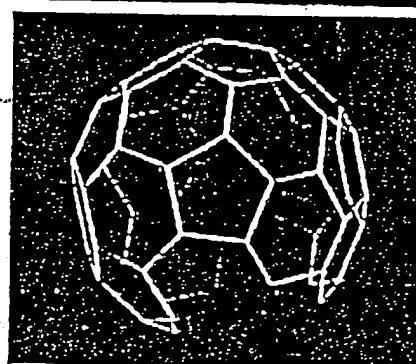
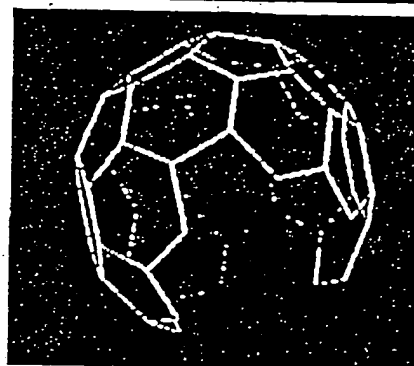
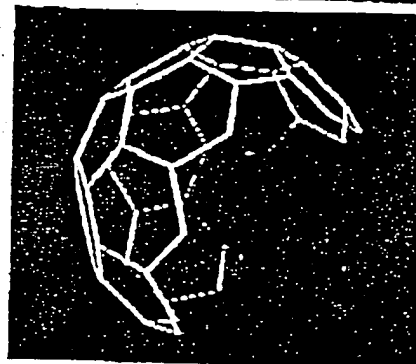
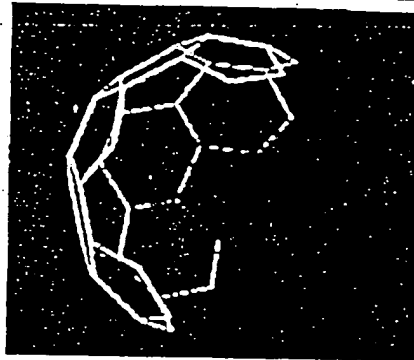
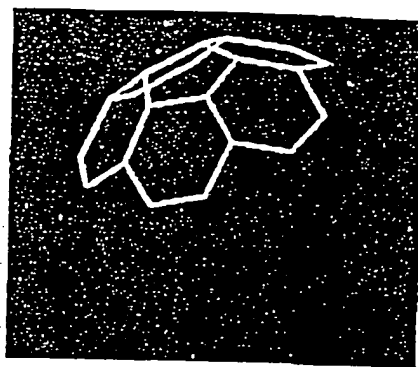
We now believe the answers to these questions lie in the way carbon vapor condenses at high temperatures. Linear carbon chains appear to link together to form graphitic sheets, and the sheets anneal as they grow in the hot vapor. Finally, stable, cage-like structures are favored by a key concept, which we call the pentagon rule.

Scientists had long known that when carbon is vaporized, most of its atoms initially coalesce into clusters ranging from two to 15 atoms or so. The very smallest carbon molecules are known to prefer essentially one-dimensional geometries. But clusters containing at least 10 atoms most commonly form a monocyclic ring—a kind of molecular Hula-Hoop that is especially favored at low temperatures. At very high temperatures, the rings break open to form units that comprise as many as 25 carbon atoms, taking the form of linear chains. Such chains might be imagined to look something like writhing snakes as they vibrate in the hot vapor.

It was these linear carbon chains that initially got us involved in carbon cluster studies and led to the discovery of  $C_{60}$ . Our British colleague, Harry Kroto, had theorized that the great abundance of such linear carbon chains in interstellar space may arise from chemical reactions in the outer atmospheres of carbon-rich red giant stars. In the early 1980s one of us (Smalley) had developed a supersonic cluster-beam device for the general study of small clusters composed of essentially any element in the periodic table [see "Microclusters," by Michael A. Duncan and Dennis H. Rouvray; SCIENTIFIC AMERICAN, December 1989].

We produced clusters by focusing an intense pulsed laser on a solid disk of the element to be studied. The local temperature could readily be brought above 10,000 degrees C—hotter than the surface of most stars and certainly hot enough to vaporize any known material. The resulting vapor was entrained in a powerful gust of helium, a chemi-

## Growth of a Buckyball



cally inert carrier gas, which cooled vapor so that it could condense into small clusters. As the carrier gas expanded through a nozzle into a vacuum, it generated a supersonic beam of clusters whose sizes could be measured by a mass spectrometer.

In 1984 a group at Exxon using a copy of the cluster-beam apparatus developed at Rice had been the first to study carbon clusters in this fashion. Their results strongly suggested that the linear carbon chains Kroto wanted to study were in fact being produced in abundance. In addition, they reported a bizarre pattern among the larger clusters: the distribution was strikingly lacking in the species having an odd number of atoms.

The Exxon researchers recorded but did not notice that two particular even-numbered members,  $C_{50}$  and  $C_{70}$ , were somewhat more abundant than their neighbors (see bottom illustration on page 58). The mysterious even-numbered distribution of clusters was separated from the small linear-chain distribution by what appeared to be something of a forbidden zone—a region of clusters between roughly 25 and 35 atoms in size in which few if any clusters could be detected.

The even-numbered distribution was soon discovered to result from the fullerenes. In one of our many studies of Kroto's linear carbon chains, we reproduced the Exxon results but found something quite striking about the distribution of large, even-numbered clusters. Heath, Kroto and O'Brien noticed that the 60th cluster seemed five times more abundant than any other even-numbered cluster in the range between 50 and 70 atoms. This differential was dramatically greater than anything that had been seen before.

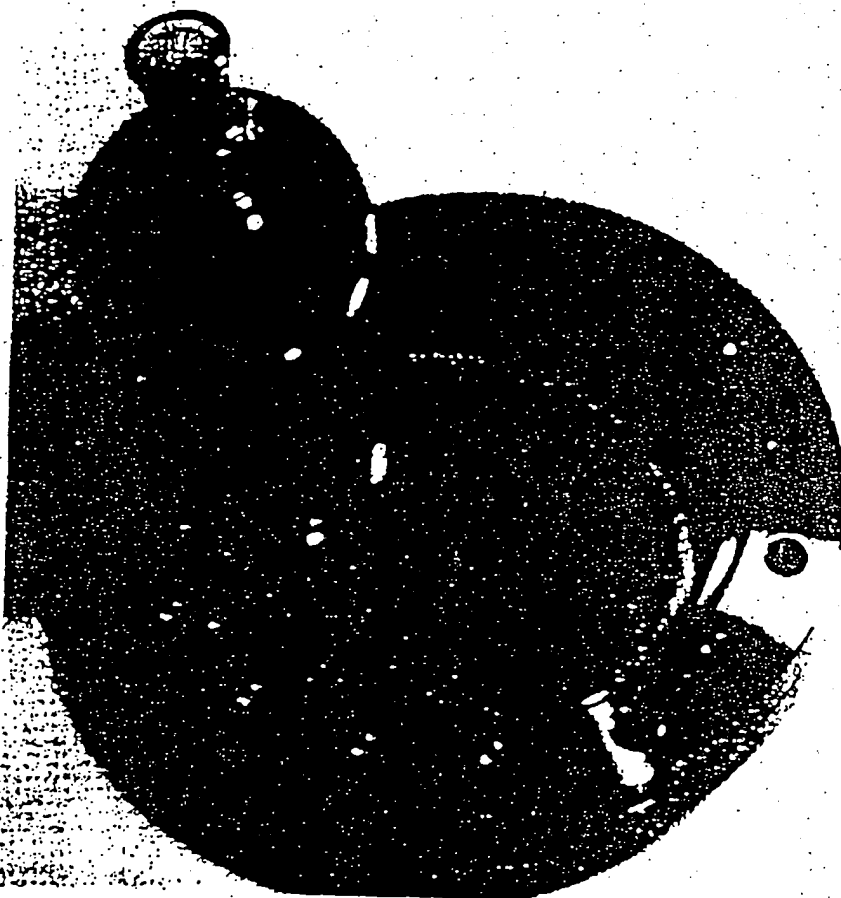
After much discussion, Heath and O'Brien spent the next weekend playing with the conditions in the laser-vaporization machine's supersonic nozzle. By Monday morning they had managed to find conditions in which  $C_{60}$  stood out in the cluster distribution like a flagpole. By the next morning we had had our Eureka! experience, and we were playing with every sort of soccerball we could get our hands on.

We found that we could explain the dominance of the even-numbered clusters by assuming they had all taken the structure of hollow, geodesic domes. They were all fullerenes. We could also argue that some fullerenes were more abundant than others because of the smoothness of the clusters' surface and the natural grouping of pentagons.

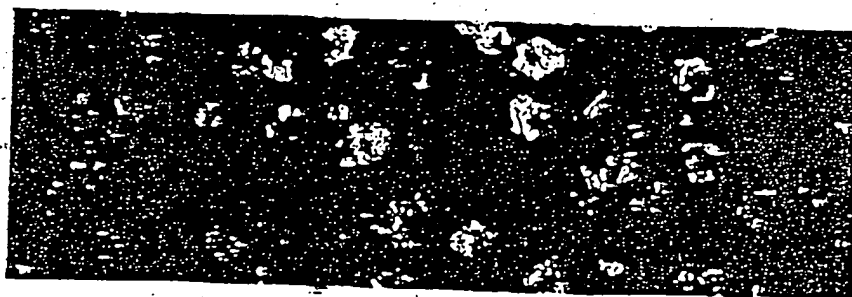
Pentagons provided an important clue. Although hundreds of examples are known in chemistry of five-membered rings attached to six-membered rings in stable aromatic compounds (for example, the nucleic acids adenine and guanine), only a few occur whose two five-membered rings share an edge. Interestingly, the smallest fullerene in which pentagons need not share an edge is  $C_{50}$ ; the next is  $C_{70}$ . Although  $C_{70}$  and all larger fullerenes can easily adopt structures in which the five-membered rings are well separated, one finds that these pentagons in the larger fullerenes occupy strained posi-

tions. This vulnerability makes the carbon atoms at such sites particularly susceptible to chemical attack.

The big question, however, was not why fullerenes were stable but rather how they formed so readily in laser-vaporized graphite. Near the end of 1985, we suggested that the process began with linear chains. As the carbon vapor began to condense, the linear chains would grow long enough to flip back on themselves to form large monocyclic Hula-Hoops. As the growth continued, the chains would also fold into more effectively connected polycyclic network structures. Because graphite,



COLOR OF  $C_{60}$  depends on its form. This yellow film was sublimed onto a glass window that had been bolted to a vacuum oven. The benzene solution is magenta.



FULLERENE CRYSTALS were produced by evaporating a benzene solution of  $C_{60}$  containing a significant admixture of  $C_{70}$ .

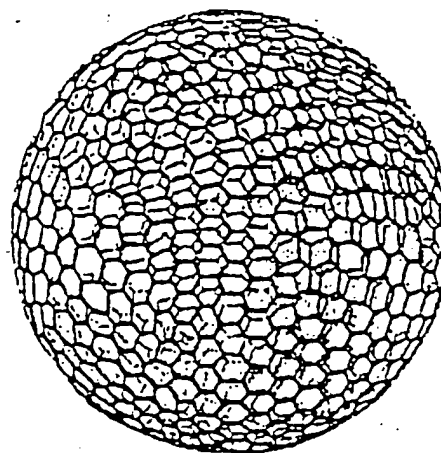
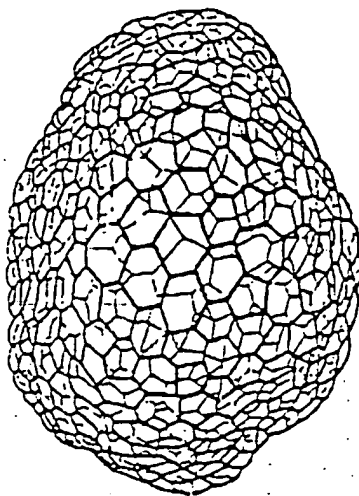
graphitic sheet structures as flat. After all, the sheets are certainly flat in a perfect crystal of graphite, and there is a huge class of very stable polycyclic aromatic hydrocarbons that are also flat (naphthalene and anthracene, for instance). But these free-floating graphitic sheets in the condensing carbon vapor have no atoms to tie up the dangling bonds on their edges. They therefore have little reason to remain flat. Indeed, the physical tendency to reach the lowest energy level available induces the sheets to eliminate their dangling bonds by curling up.

We discovered a strategy—the pentagon rule—according to which the sheets could accomplish this feat. The sheets rearrange their bonding so that pentagons are formed, causing the network to curve and permitting at least one good carbon-carbon bond to replace two dangling bonds. If some pentagons were good, more would be better. But we cautioned that it would be wise to avoid having two pentagons positioned so that they shared an edge, since this configuration is known to be rather unstable. If this process continues as the graphitic sheet grows, the network will naturally curl until the opposing edges meet to form the perfect soccerball structure. In this way, we argued in 1985, the formation of buckminsterfullerene from spontaneously condensing carbon vapor might not be so surprising after all.

Of course, there is no reason to expect that all growing graphitic sheets will close up—they merely have a theoretical propensity to do so. In reality, we expected clusters to grow too fast for imperfections to be corrected, so that the growing edge would typically overrun the opposite side, much like an overgrown toenail. Further growth would result in a spiraling nautilus-shaped structure that would prevent the growing edge from ever meeting its opposite, which would be hopelessly buried on the inside of the spiral.

This spiral shape seemed so interesting that we went on to suggest it may be formed in sooting flames and may in fact be the nucleus involved in the formation of soot. In this scenario, fullerenes like  $C_{60}$  and  $C_{70}$  are rather unlikely local stopping points in a curving, spiraling growth mechanism that ultimately results in soot.

Although this turned out to be a useful model, which within a few years led to the discovery that  $C_{60}$  and the other fullerenes are in fact abundant in all sooting flames, to some extent it misled us. Perfect closure need not always be that unlikely. Granted, the curving process is liable to be waylaid in a can-



**LIVING FULLERENES:** these radiolarians—protozoans having siliceous skeletons—appear in D'Arcy Thompson's 1917 classic, *On Growth and Form*.

dle flame, where much hydrogen wanders around, tying up dangling bonds as it goes. These terminated dangling bonds would tend to frustrate the curving and closing mechanism.

But in a pure condensing carbon vapor one may be able to prolong the period in which the carbon nets remain open. If the temperature is kept high enough, the nets will effectively anneal, that is, they will adopt their most favored form by obeying the pentagon rule. Such conditions should thus produce a very high yield of  $C_{60}$ . This is what we believe Krätschmer and Huffman achieved. By using a simple, resistively heated graphite rod, they ensured that the concentration of small linear carbon radicals would be low and that the graphitic sheets would add these chains to their edges relatively slowly. The helium was critical, we believe, because it slowed migration of these chains away from the graphite rod. More chains lingered near the arc, which provided the heat they needed to continue to curve.

Not only was this line of reasoning available to us in 1985, it was a direct extension of the growth model we proposed at the time. Yet the yellow vial, so close to our grasp, eluded us because we did not think big. We were so intent on proving the existence of soccerball molecules that we asked no more of our model than that it rationalize tiny yields of  $C_{60}$ . Had we asked for more, had we considered the model's logical consequences, we would have—at least we should have—realized that we were heating and cooling the carbon too fast for it to anneal properly.

The solution would then have become obvious: the whole apparatus must be

heated so that the laser-vaporized carbon plume expands further while it is still hot enough to anneal. Sure enough, when we finally did this in November 1990 by keeping the graphite target in an oven at 1,200 degrees C while passing helium over it slowly, a yellow-brown film of  $C_{60}$  and  $C_{70}$  rapidly sublimed on the surface of the oven. We found what we were looking for—five years late.

It appears, therefore, that a rather simple model explains the ready formation of this brand-new class of carbon molecules. Amazingly,  $C_{60}$  appears to result inevitably when carbon condenses slowly enough and at a high enough temperature. This discovery has come a bit later than it should have. But no matter: now we have it. And now the real fun can begin!

#### FURTHER READING

- PROBING  $C_{60}$ .** Robert F. Curl and Richard E. Smalley in *Science*, Vol. 242, pages 1017-1022; November 18, 1988.
- SPACE, STARS,  $C_{60}$ , AND SOOT.** Harold Kroto in *Science*, Vol. 242, pages 1139-1143; November 25, 1988.
- GREAT BALLS OF CARBON: THE STORY OF BUCKMINSTERFULLERENE.** Richard E. Smalley in *The Sciences*, Vol. 31, No. 2, pages 22-28; March/April 1991.
- STRUCTURE OF SINGLE-PHASE SUPERCONDUCTING  $K_3C_{60}$ .** Peter W. Stephens, Laszlo Mihaly, Peter L. Lee, Robert L. Whetten, Shihou-Mei Huang, Richard Kaner, François Delidrich and Karoly Holczner in *Nature*, Vol. 351, No. 6328, pages 632-634; June 20, 1991.
- FULLERENES  $C_{60}$  AND  $C_{70}$  IN FLAMES.** Jack B. Howard, J. Thomas McClinnon, Yakov Makarovskiy, Arthur L. Lafleur and M. Elaine Johnson in *Nature*, Vol. 352, No. 6331, pages 139-141; July 11, 1991.

the most stable known form of carbon, has its atoms bound in infinite hexagonal sheets, we suspected that the polycyclic network clusters resembled pieces of such sheets. We expected it to look like a fragment of chicken wire.

Like a cutout section of chicken wire,

these graphitic sheets would have many dangling bonds, making them chemically reactive—much more so than the smaller linear chains, which have only two such bonds, one on each end. The sheets, therefore, would not be expected to be abundant in the cluster beams.

Almost as soon as they form, they react with other small carbon molecules and grow too large to be seen. This, we believe, explains why there is a forbidden zone between the small linear-chain distribution and the first small fullerenes.

Chemists are conditioned to think of

## Fullerene Electronics

**C**urrently the most technologically interesting properties of bulk  $C_{60}$  are electronic: In various compound forms it functions as an insulator, a conductor, a semiconductor and a superconductor.

The material crystallizes when  $C_{60}$  molecules pack together like Ping-Pong balls in a face-centered cubic lattice. Calculations over the past few months have predicted that this new material is a direct band-gap semiconductor like gallium arsenide. All its units stand precisely at their posts in a crystalline structure. But unlike the elements of gallium arsenide, the buckyballs spin freely and at random. This disorder gives them a certain resemblance to amorphous silicon—a constituent of inexpensive solar cells. The peculiar disorder within order of bulk  $C_{60}$  has yet to be fully explored, but it is expected to produce a wholly new kind of semiconductor.

Early in 1991 researchers at AT&T Bell Laboratories discovered that they could mix, or dope,  $C_{60}$  with potassium to produce a new metallic phase—a "buckide" salt. It reaches its maximum electrical conductivity when there are three potassium atoms to each buckyball. If too much potassium is added, however, the material becomes insulating. Subsequent work has shown that  $K_3C_{60}$  is a stable metallic crystal consisting of a face-centered cubic structure of buckyballs, with potassium ions filling the cavities between the balls. Potassium buckide is the first completely three-dimensional molecular metal.

The Bell Labs team further discovered that this  $K_3C_{60}$  metal becomes a superconductor when cooled below 18 kelvins. When rubidium is substituted for the potassium, the critical temperature for superconductivity was found to be near 30 kelvins. (Recently workers at Allied-Signal, Inc., detected superconductivity at 43 kelvins for rubidium-thallium-doped material.) Careful work at the University of California at Los Angeles has shown that the superconducting phase is stable and readily annealed—imperfections can be smoothed away by heating and cooling.

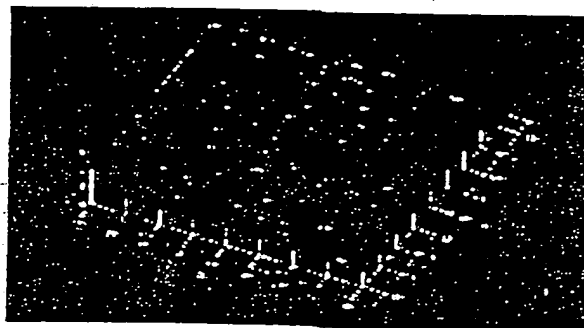
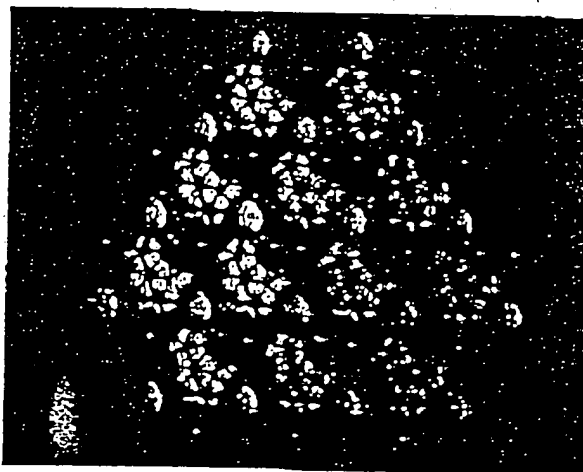
The material can therefore be manufactured as a three-dimensional superconductor, making it a candidate for practical superconducting wires. Early estimates of magnetic and other characteristics indicate that these superconducting buckide salts are similar to the high-temperature superconducting ceramics made of yttrium, barium and copper oxide.

Recent work at the University of Minnesota has shown that highly ordered  $C_{60}$  films can readily be grown on crystalline substrates, such as gallium arsenide. This attribute makes the film a suitable material for microelectronic fabrication. Beautifully regular films of the  $K_3C_{60}$  superconductor can also be made [see micrograph at right], and the interface between the  $C_{60}$  crystalline film and the  $K_3C_{60}$  material has been found to be stable. It may thus lend itself to the production of intricately layered microelectronic devices.

In order for the semiconducting properties of fullerene materials to be thoroughly exploited, scientists need to

learn how to dope them selectively to make *n*-type and *p*-type fullerene films, which donate electrons and holes, respectively. Such doping may involve putting a dopant atom inside the cage, either by growing the cage around the atom or by shooting atoms through the carbon walls by brute force. Small atoms, such as helium, have already been injected this way into the  $C_{60}$  cage, and it seems likely that hydrogen and lithium are insertable as well.

The versatility of bulk  $C_{60}$  seems to grow week by week. As we go to press, for example, there is a report suggesting that fullerene complexes exhibit ferromagnetic qualities in the absence of metals, an unparalleled phenomenon. Also, British workers from the universities of Leicester, Southampton and Sussex have just reported the generation of macroscopic quantities of fully fluorinated buckyballs ( $C_{60}F_{60}$ ). The resulting "teflon balls" may be among the world's best lubricants. We do not know what the fullerenes' burgeoning traits will allow, but it would be surprising if the possibilities are not wonderful.



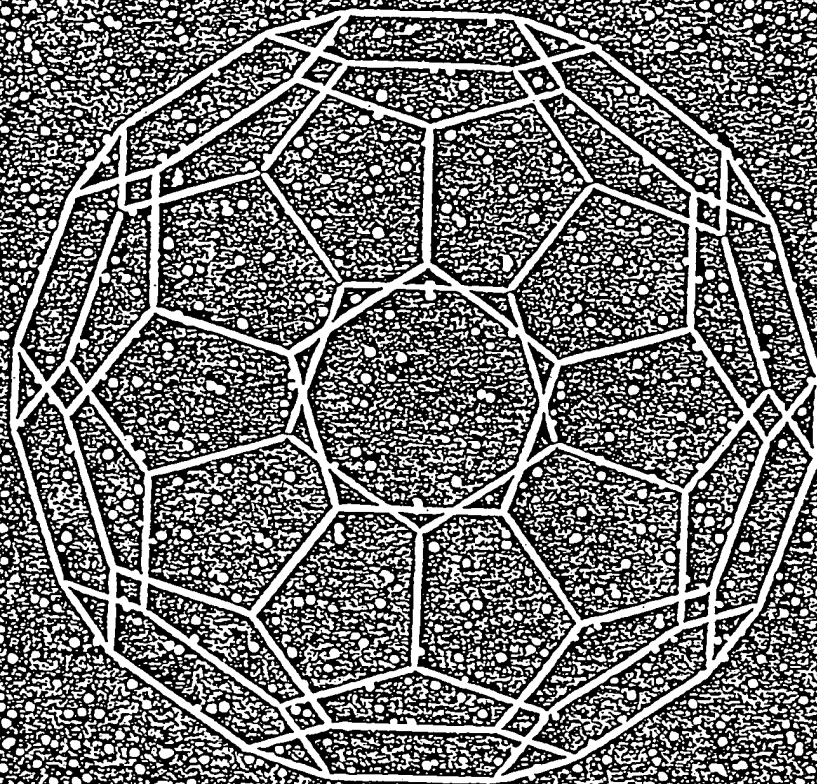
**SUPERCONDUCTING FULLERIDE** forms when buckyballs are doped with potassium in the ratio of  $K_3C_{60}$  (diagram), producing a crystal that can be grown on a gallium arsenide substrate (scanning tunneling micrograph).

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## SIXTY-CARBON CLUSTER

### AUTUMN BOOKS

Harvey Brooks  
(transformation of MIT)

P. N. Johnson-Laird  
(brain and mind)

Anthony W. Clare  
(psychoanalysis as religion)

A. O. Lucas  
(war on disease)

Hendrik B. G. Casimir  
(physics and physicists)

Gordon Thompson  
(dimensions of nuclear proliferation)

Jacques Ninio  
(origins of life)

Edward Harrison  
(steps through the cosmos)



# $C_{60}$ : Buckminsterfullerene

H. W. Kroto<sup>\*</sup>, J. R. Heath, S. C. O'Brien, R. F. Curl  
& R. E. Smalley

Rice Quantum Institute and Departments of Chemistry and Electrical Engineering, Rice University, Houston, Texas 77251, USA

During experiments aimed at understanding the mechanisms by which long-chain carbon molecules are formed in interstellar space and circumstellar shells<sup>1</sup>, graphite has been vaporized by laser irradiation, producing a remarkably stable cluster consisting of 60 carbon atoms. Concerning the question of what kind of 60-carbon atom structure might give rise to a superstable species, we suggest a truncated icosahedron, a polygon with 60 vertices and 32 faces, 12 of which are pentagonal and 20 hexagonal. This object is commonly encountered as the football shown in Fig. 1. The  $C_{60}$  molecule which results when a carbon atom is placed at each vertex of this structure has all valences satisfied by two single bonds and one double bond, has many resonance structures, and appears to be aromatic.

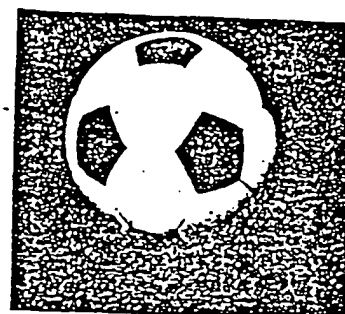
The technique used to produce and detect this unusual molecule involves the vaporization of carbon species from the surface of a solid disk of graphite into a high-density helium flow using a focused pulsed laser. The vaporization laser was the second harmonic of Q-switched Nd:YAG producing pulse energies of ~30 mJ. The resulting carbon clusters were expanded in a supersonic molecular beam, photoionized using an excimer laser, and detected by time-of-flight mass spectrometry. The vaporization chamber is shown in Fig. 2. In the experiment the pulsed valve was opened first and then the vaporization laser was fired after a precisely controlled delay. Carbon species were vaporized into the helium stream, cooled and partially equilibrated in the expansion, and travelled in the resulting molecular beam to the ionization region. The clusters were ionized by direct one-photon excitation with a carefully synchronized excimer laser pulse. The apparatus has been fully described previously<sup>2-3</sup>.

The vaporization of carbon has been studied previously in a very similar apparatus<sup>6</sup>. In that work clusters of up to 190 carbon atoms were observed and it was noted that for clusters of more than 40 atoms, only those containing an even number of atoms were observed. In the mass spectra displayed in ref. 6, the  $C_{60}$  peak is the largest for cluster sizes of >40 atoms, but it is not completely dominant. We have recently re-examined this system and found that under certain clustering conditions the  $C_{60}$  peak can be made about 40 times larger than neighbouring clusters.

Figure 3 shows a series of cluster distributions resulting from variations in the vaporization conditions evolving from a cluster distribution similar to that observed in ref. 3, to one in which  $C_{60}$  is totally dominant. In Fig. 3c, where the firing of the vaporization laser was delayed until most of the He pulse had passed, a roughly gaussian distribution of large, even-numbered clusters with 38-120 atoms resulted. The  $C_{60}$  peak was largest but not dominant. In Fig. 3b, the vaporization laser was fired at the time of maximum helium density; the  $C_{60}$  peak grew into a feature perhaps five times stronger than its neighbours, with the exception of  $C_{70}$ . In Fig. 3a, the conditions were similar to those in Fig. 3b but in addition the integrating cup depicted in Fig. 2 was added to increase the time between vaporization and expansion. The resulting cluster distribution is completely dominated by  $C_{60}$ , in fact more than 50% of the total large cluster abundance is accounted for by  $C_{60}$ ; the  $C_{70}$  peak has diminished in relative intensity compared with  $C_{60}$ , but remains rather prominent, accounting for ~5% of the large cluster population.

Our rationalization of these results is that in the laser vaporization, fragments are torn from the surface as pieces of the planar

Fig. 1 A football (in the United States, a soccerball) on Texas grass. The  $C_{60}$  molecule featured in this letter is suggested to have the truncated icosahedral structure formed by replacing each vertex on the seams of such a ball by a carbon atom.



graphite fused six-membered ring structure. We believe that the distribution in Fig. 3c is fairly representative of the nascent distribution of larger ring fragments. When these hot ring clusters are left in contact with high-density helium, the clusters equilibrate by two- and three-body collisions towards the most stable species, which appears to be a unique cluster containing 60 atoms.

When one thinks in terms of the many fused-ring isomers with unsatisfied valences at the edges that would naturally arise from a graphite fragmentation, this result seems impossible: there is not much to choose between such isomers in terms of stability. If one tries to shift to a tetrahedral diamond structure, the entire surface of the cluster will be covered with unsatisfied valences. Thus a search was made for some other plausible structure which would satisfy all  $sp^2$  valences. Only a spheroidal structure appears likely to satisfy this criterion, and thus Buckminster Fuller's studies were consulted (see, for example, ref. 7). An unusually beautiful (and probably unique) choice is the truncated icosahedron depicted in Fig. 1. As mentioned above, all valences are satisfied with this structure, and the molecule appears to be aromatic. The structure has the symmetry of the icosahedral group. The inner and outer surfaces are covered with a sea of  $\pi$  electrons. The diameter of this  $C_{60}$  molecule is ~7 Å, providing an inner cavity which appears to be capable of holding a variety of atoms<sup>8</sup>.

Assuming that our somewhat speculative structure is correct, there are a number of important ramifications arising from the existence of such a species. Because of its stability when formed under the most violent conditions, it may be widely distributed in the Universe. For example, it may be a major constituent of circumstellar shells with high carbon content. It is a feasible constituent of interstellar dust and a possible major site for

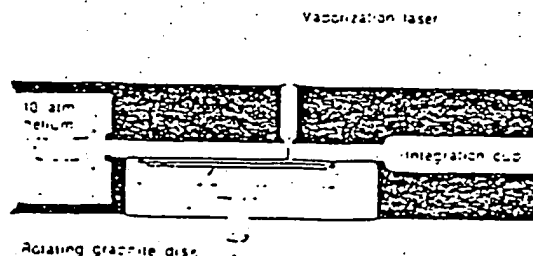


Fig. 2 Schematic diagram of the pulsed supersonic nozzle used to generate carbon cluster beams. The integrating cup can be removed at the indicated line. The vaporization laser beam (30-40 mJ at 532 nm in a 5-ns pulse) is focused through the nozzle, striking a graphite disk which is rotated slowly to produce a smooth vaporization surface. The pulsed nozzle passes high-density helium over this vaporization zone. This helium carrier gas provides the thermalizing collisions necessary to cool, react and cluster the species in the vaporized graphite plasma, and the wind necessary to carry the cluster products through the remainder of the nozzle. Free expansion of this cluster-laden gas at the end of the nozzle forms a supersonic beam which is probed 1.3 m downstream with a time-of-flight mass spectrometer.

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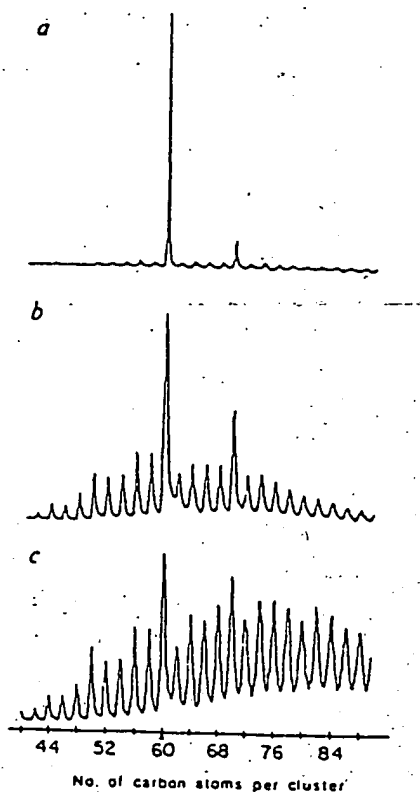


Fig. 3 Time-of-flight mass spectra of carbon clusters prepared by laser vaporization of graphite and cooled in a supersonic beam. Ionization was effected by direct one-photon excitation with an ArF excimer laser (6.4 eV,  $1 \text{ mJ cm}^{-2}$ ). The three spectra shown differ in the extent of helium collisions occurring in the supersonic nozzle. In c, the effective helium density over the graphite target was less than 10 torr—the observed cluster distribution here is believed to be due simply to pieces of the graphite sheet ejected in the primary vaporization process. The spectrum in b was obtained when roughly 760 torr helium was present over the graphite target at the time of laser vaporization. The enhancement of  $\text{C}_{60}$  and  $\text{C}_{70}$  is believed to be due to gas-phase reactions at these higher clustering conditions. The spectrum in a was obtained by maximizing these cluster thermalization and cluster-cluster reactions in the 'integration cup' shown in Fig. 2. The concentration of cluster species in the especially stable  $\text{C}_{60}$  form is the prime experimental observation of this study.

surface-catalysed chemical processes which lead to the formation of interstellar molecules. Even more speculatively,  $\text{C}_{60}$  or a derivative might be the carrier of the diffuse interstellar lines<sup>9</sup>.

If a large-scale synthetic route to this  $\text{C}_{60}$  species can be found, the chemical and practical value of the substance may prove extremely high. One can readily conceive of  $\text{C}_{60}$  derivatives of many kinds—such as  $\text{C}_{60}$  transition metal compounds, for example,  $\text{C}_{60}\text{Fe}$  or halogenated species like  $\text{C}_{60}\text{F}_{60}$  which might be a super-lubricant. We also have evidence that an atom (such as lanthanum<sup>8</sup> and oxygen<sup>1</sup>) can be placed in the interior, producing molecules which may exhibit unusual properties. For example, the chemical shift in the NMR of the central atom should be remarkable because of the ring currents. If stable in macroscopic, condensed phases, this  $\text{C}_{60}$  species would provide a topologically novel aromatic nucleus for new branches of organic and inorganic chemistry. Finally, this especially stable and symmetrical carbon structure provides a possible catalyst and/or intermediate to be considered in modelling prebiotic chemistry.

We are disturbed at the number of letters and syllables in the rather fanciful but highly appropriate name we have chosen in the title to refer to this  $\text{C}_{60}$  species. For such a unique and centrally important molecular structure, a more concise name would be useful. A number of alternatives come to mind (for example, ballene, spherene, soccerene, carbosoccer), but we prefer to let this issue of nomenclature be settled by consensus.

We thank Frank Tittel, Y. Liu and Q. Zhang for helpful discussions, encouragement and technical support. This research was supported by the Army Research Office and the Robert A. Welch Foundation, and used a laser and molecular beam apparatus supported by the NSF and the US Department of Energy. H.W.K. acknowledges travel support provided by SERC, UK. J.R.H. and S.C.O'B. are Robert A. Welch Predoctoral Fellows.

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# The Nobel Prize in Chemistry 1996

"for their discovery of fullerenes"

Press release

The Fullerene Gallery

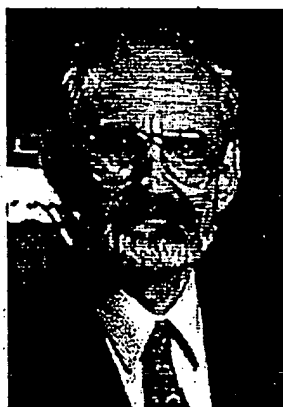
**Robert F. Curl, Jr.**

USA

Rice University  
Houston, USA

1933 -

Autobiography



**Sir Harold W. Kroto**

U.K.

University of Sussex,  
Brighton, U.K.

1939 -

Autobiography



**Richard E. Smalley**

USA

Rice University,  
Houston, USA

1943 -

Autobiography

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## Press Release: The 1996 Nobel Prize in Chemistry

### KUNGL. VETENSKAPSAKADEMIEN THE ROYAL SWEDISH ACADEMY OF SCIENCES

9 October 1996

The Royal Swedish Academy of Sciences has decided to award the 1996 Nobel Prize in Chemistry to

Professor **Robert F. Curl, Jr.**, Rice University, Houston, USA,  
Professor **Sir Harold W. Kroto**, University of Sussex, Brighton, U.K., and  
Professor **Richard E. Smalley**, Rice University, Houston, USA,

**for their discovery of fullerenes.**

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Note: This document is made for Netscape 2.0 or later, and some of the chemical formulas might not appear as intended using other browsers.

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#### **The discovery of carbon atoms bound in the form of a ball is rewarded**

New forms of the element carbon - called fullerenes - in which the atoms are arranged in closed shells was discovered in 1985 by **Robert F. Curl, Harold W. Kroto** and **Richard E. Smalley**. The number of carbon atoms in the shell can vary, and for this reason numerous new carbon structures have become known. Formerly, six crystalline forms of the element carbon were known, namely two kinds of graphite, two kinds of diamond, chaoit and carbon(VI). The latter two were discovered in 1968 and 1972.

Fullerenes are formed when vaporised carbon condenses in an atmosphere of inert gas. The gaseous carbon is obtained e.g. by directing an intense pulse of laser light at a carbon surface. The released carbon atoms are mixed with a stream of helium gas and combine to form clusters of some few up to hundreds of atoms. The gas is then led into a vacuum chamber where it expands and is cooled to some degrees above absolute zero. The carbon clusters can then be analysed with mass spectrometry.

Curl, Kroto and Smalley performed this experiment together with graduate students J.R. Heath and S.C. OBrien during a period of eleven days in 1985. By fine-tuning the experiment they were able in particular to produce clusters with 60 carbon atoms and clusters with 70. Clusters of 60 carbon atoms,  $C_{60}$ , were the most abundant. They found high stability in  $C_{60}$ , which suggested a molecular structure of great symmetry. It was suggested that  $C_{60}$  could be a "truncated icosahedron cage", a polyhedron with 20 hexagonal (6-angled) surfaces and 12 pentagonal (5-angled) surfaces. The pattern of a European football has exactly this structure, as does the geodetic dome designed by the American architect R. Buckminster Fuller for the 1967 Montreal World Exhibition. The researchers named the newly-discovered structure *buckminsterfullerene* after him.

The discovery of the unique structure of the  $C_{60}$  was published in the journal *Nature* and had a mixed reception - both criticism and enthusiastic acceptance. No physicist or chemist had expected that carbon would be found in such a symmetrical form other than those already known. Continuing their work during 1985-90, Curl, Kroto and Smalley obtained further evidence that the proposed structure ought to be correct. Among other things they succeeded in identifying carbon clusters that enclosed one or more metal atoms. In 1990 physicists W. Krätschmer and D.R. Huffman for the first time produced isolable quantities of  $C_{60}$  by causing an arc between two graphite rods to burn in a helium atmosphere and extracting the carbon condensate so formed using an organic solvent. They obtained a mixture of  $C_{60}$  and  $C_{70}$ , the structures of which could be determined. This confirmed the correctness of the  $C_{60}$  hypothesis. The way was thus open for studying the chemical properties of  $C_{60}$  and other carbon clusters such as  $C_{70}$ ,  $C_{76}$ ,  $C_{78}$  and  $C_{84}$ . New substances were produced from these compounds, with new and unexpected properties. An entirely new branch of chemistry developed, with consequences in such diverse areas as astrochemistry, superconductivity and materials chemistry/physics.

### Background

Many widely diverse research areas coincide in the discovery of the fullerenes. **Harold W. Kroto** was at the time active in microwave spectroscopy, a science which thanks to the growth of radioastronomy can be used for analysing gas in space, both in stellar atmospheres and in interstellar gas clouds. Kroto was particularly interested in carbon-rich giant stars. He had discovered and investigated spectrum lines in their atmospheres and found that they could be ascribed to a kind of long-chained molecule of only carbon and nitrogen, termed cyanopolyynes. The same sort of molecules is also found in interstellar gas clouds. Kroto's idea was that these carbon compounds had been formed in stellar atmospheres, not in clouds. He now wished to study the formation of these long-chain molecules more closely.

He got in touch with **Richard E. Smalley**, whose research was in cluster chemistry, an important part of chemical physics. A cluster is an aggregate of atoms or molecules, something in between microscopic particles and macroscopic particles. Smalley had designed and built a special *laser-supersonic cluster beam apparatus* able to vaporise almost any known material into a plasma of atoms and study the design and distribution of the clusters. His paramount interest was clusters of metal atoms, e.g. metals included in semiconductors, and he often performed these investigations together with **Robert F. Curl**, whose background was in microwave and infra-red spectroscopy.

### Atoms form clusters

When atoms in a gas phase condense to form clusters, a series is formed where the size of the clusters varies from a few atoms to many hundreds. There are normally two size maxima visible in the distribution curve, one around small clusters and one around large. It is often found that certain cluster sizes may dominate, and the number of atoms in these is termed a "magic number", a term borrowed from nuclear physics. These dominant cluster sizes were assumed to have some special property such as high symmetry.

### Fruitful contact

Through his acquaintanceship with Robert Curl, Kroto learned that it should be possible to use Smalley's instrument to study the vaporisation and cluster formation of carbon, which might afford him evidence that the long-carbon-chain compounds could have been formed in the hot parts of stellar atmospheres. Curl conveyed this interest to Smalley and the result was that on 1 September 1985 Kroto arrived in Smalley's laboratory to start, together with Curl and Smalley, the experiments on carbon vaporisation. In the course of the work it proved possible to influence drastically the size distribution of the carbon clusters where, predominantly, 60 appeared as a magic number but also 70 (Fig. 1). The research group

now got something else to think about. Instead of long carbon chains, the idea arose that the  $C_{60}$  cluster could have the structure of a truncated (cut off) icosahedron (Fig. 2) since its great stability was assumed to correspond to a closed shell with a highly symmetrical structure.  $C_{60}$  was given a fanciful name, buckminsterfullerene, after the American architect R. Buckminster Fuller, inventor of the geodesic dome. This hectic period ended on 12 September with the despatch of a manuscript entitled  $C_{60}$ : *Buckminsterfullerene* to *Nature*. The journal received it on 13 September and published the article on 14 November 1985.

### Sensational news

For chemists the proposed structure was uniquely beautiful and satisfying. It corresponds to an aromatic, three-dimensional system in which single and double bonds alternated, and was thus of great theoretical significance. Here, moreover, was an entirely new example from a different research tradition with roots in organic chemistry: producing highly symmetrical molecules so as to study their properties. The Platonic bodies have often served as patterns, and hydrocarbons had already been synthesised as tetrahedral, cubic or dodecahedral (12-sided) structures.

### Carbon atoms per cluster

#### Fig. 1

Using mass spectroscopy it was found that the size distribution of carbon clusters could be drastically affected by increasing the degree of chemical "boiling" in the inlet nozzle to the vacuum chamber. Clusters with 60 and 70 carbon atoms could be produced. (Acc. Chem. Res., Vol. 25, No. 3, 1992)

#### Fig. 2

Models of the structures of  $C_{60}$ . (Acc. Chem. Res., Vol. 25, No. 3, 1992)

### Further investigations

To gain further clarity Curl, Kroto and Smalley continued their investigations of  $C_{60}$ . They attempted to make it react with other compounds. Gases such as hydrogen, nitrous oxide, carbon monoxide, sulphur dioxide, oxygen or ammonia were injected into the gas stream, but no effect on the  $C_{60}$  peak recorded in the mass spectrometer could be demonstrated. This showed that  $C_{60}$  was a slow-reacting compound. It also turned out that all carbon clusters with an even number of carbon atoms from 40-80 (the interval that could be studied) reacted equally slowly. Analogously with  $C_{60}$  all these should then correspond to entirely closed structures, resembling cages. This was in agreement with Euler's law, a mathematical proposition which states that for any polygon with  $n$  edges, where  $n$  is an even number greater than 22, at least one polyhedron can be constructed with 12 pentagons and  $(n-20)/2$  hexagons, which, in simple terms, states that it is possible with 12 pentagons and with none or more than one hexagon to construct a polyhedron. For large  $n$  many different closed structures can occur, thus also for  $C_{60}$ , and it was presumably the beautiful symmetry of the proposed structure that gave it the preference.

The combination of chemical inertia in clusters with even numbers of carbon atoms and the possibility that all these could possess closed structures in accordance with Euler's law, led to the proposal that all these carbon clusters should have closed structures. They were given the name fullerenes and conceivably an almost infinite number of fullerenes could exist. The element carbon had thus assumed an almost infinite number of different structures.

### $C_{60}$ and metals

New experiments were rapidly devised to test the  $C_{60}$  hypothesis. Since the  $C_{60}$  structure is hollow, with room for one or more other atoms, attempts were made to enclose a metal atom. A graphite sheet was soaked with a solution of a metal salt (lanthanum chloride,  $LaCl_3$ ) and subjected to vaporisation-condensation experiments. Massspectroscopic analysis of the clusters formed showed the presence of  $C_{60}La^+$ . These proved to be photoresistant, i.e. irradiation with intense laser light did not remove the metal atoms. This reinforced the idea that metal atoms were captured inside the cage structure.

The possibility of producing clusters with a metal atom enclosed gave rise to what was termed the "shrink-wrapping" experiment. Ions of one and the same size or at least similar sizes were gathered in a magnetic trap and subjected to a laser pulse. It then turned out that the laser beam caused the carbon cage to shrink by 2 carbon atoms at a time: at a certain cage size, when the pressure on the metal atom inside

became too great, the fragmentation ceased. The shell had then shrunk so that it fitted exactly around the metal atom. For  $C_{60}Cs^+$  this size was at  $C_{48}Cs^+$ , for  $C_{60}K^+$  it was at  $C_{44}K^+$  and for  $C_{60}^+$  at  $C_{32}^+$ .

#### Further strong evidence gave rise to new chemistry

At the end of the 1980s, strong evidence was available that the  $C_{60}$  hypothesis was correct. In 1990 the synthesis of macroscopic quantities of  $C_{60}$  through carbon arc vaporisation between two graphite electrodes permitted the attainment of full certainty - the whole battery of methods for structure determination could be applied to  $C_{60}$  and other fullerenes and completely confirmed the fullerene hypothesis. As opposed to the other forms of carbon the fullerenes represent well-defined chemical compounds with in some respects new properties. A whole new chemistry has developed to manipulate the fullerene structure, and the properties of fullerenes can be studied systematically. It is possible to produce superconducting salts of  $C_{60}$ , new three-dimensional polymers, new catalysts, new materials and electrical and optical properties, sensors, and so on. In addition, it has been possible to produce thin tubes with closed ends, nanotubes, arranged in the same way as fullerenes. From a theoretical viewpoint, the discovery of the fullerenes has influenced our conception of such widely separated scientific problems as the galactic carbon cycle and classical aromaticity, a keystone of theoretical chemistry. No practically useful applications have yet been produced, but this is not to be expected as early as six years after macroscopic quantities of fullerenes became available.

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Robert F. Curl Jr., was born in 1933 in Alice, Texas, USA: Ph.D. in chemistry in 1957 at University of California, Berkeley, USA. Curl has since 1958 worked at Rice University, where he has been a professor since 1967.

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**Richard E. Smalley** was born in 1943 in Akron, Ohio, USA. Ph.D. in chemistry 1973 at Princeton University, USA. Professor of Chemistry at Rice University since 1981 and also Professor of Physics at the same university since 1990. Member of the National Academy of Sciences in the USA and other bodies.

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